OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT INITIATION

Date: August 6, 1976

Project Title: Utilization and Stabilization of Pyrolytic Oils from Pyrolysis of Agricultural, Municipal, and Other Wastes

Project No: B-469 Green card.

Project Director: Dr. James A. Knight

Sponsor: Environmental Protection Agency

Agreement Period: From June 21, 1976 Until June 20,1977

Type Agreement: Grant No. R804416010

Amount: $61,750 EPA
3,250 GIT (E-___-___)
$65,000 Total

Reports Required: Quarterly Progress Reports; Final Report

Sponsor Contact Person (s):

Technical Matters

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Contractual Matters

~~(thru OCA)~~
Grants Officer
Environmental Protection Agency
Grants Administration Division
401 M Street, S.W.
Washington, D. C. 20460

Defense Priority Rating: None

Assigned to: Productivity/Technology Applications (~~School~~/Laboratory)

COPIES TO:

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- Project Code (GTRI)
- Other ___

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: September 20, 1979

Project Title: Utilization and Stabilization of Pyrolytic Oils from Pyrolysis of Agricultural, Municipal, and Other Wastes.

Project No: B-469 (Continued by B-531)

Project Director: Dr. James A. Knight

Sponsor: Environmental Protection Agency; Cincinnati, OH 45268

Effective Termination Date: 10/1/78

Clearance of Accounting Charges: 10/1/78

Grant/Contract Closeout Actions Remaining:

NONE

_ Final Invoice and Closing Documents
_ Final Fiscal Report
_ Final Report of Inventions
_ Govt. Property Inventory & Related Certificate
_ Classified Material Certificate
_ Other _____

Assigned to: CMSL/PDG (School/Laboratory)

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CA–4 (1/79)

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

Atlanta, Georgia

Quarterly Report No. 1

June 21, 1976--Sept. 30, 1976

Project B-469

UTILIZATION AND/OR STABILIZATION OF PYROLYTIC OIL FROM PYROLYSIS OF AGRICULTURAL, MUNICIPAL AND OTHER WASTES

by

J. A. Knight

Grant No. R 804 416 010

Performed for

Municipal Environmental Research Laboratory

Environmental Protection Agency

Cincinnati, Ohio 45268

PROJECT B-469

UTILIZATION AND/OR STABILIZATION OF PYROLYTIC OIL FROM PYROLYSIS OF AGRICULTURAL, MUNICIPAL AND OTHER WASTES

SUMMARY

The major portion of the literature search has been completed, and the references are currently being evaluated for relevance to this project. The current literature will be searched for pertinent information and data during the period of this project. More detailed information on the results of the literature search will be included in the next quarterly report.

Pyrolytic oil for this investigation was obtained in July from the operation of the Tech-Air facility, which is a 50 dry tons/day pyrolysis system. The facility is located in a lumber yard in Cordele, Georgia, and processes a pine bark-sawdust mixture. The feed material and pyrolytic oil have been characterized by a number of different analytical techniques.

Preliminary distillations that have been conducted with the pyrolytic oil include atmospheric, vacuum, and steam distillation. A sample of the vacuum oil distillate was fractionally distilled with a spinning band column.

Considerable effort is underway to find satisfactory analytical procedures that can be used for evaluation of the oil fractions obtained from the processing techniques. The major effort at the present time is with liquid and gas chromatography.

A technical paper, "Pyrolysis of Pine Sawdust," supported in part by this grant was presented at the national American Chemical Society meeting in San Francisco, August 29--September 3, 1976.

WORK PROGRAM FOR NEXT REPORTING PERIOD

During the next reporting period, October--December 1976, the following work is planned:

Search of current literature will be continued, and the results and evaluation of the initial literature search will be summarized.

Physical processing of the pyrolytic oil will be continued with emphasis on distillation techniques.

The work with liquid and gas chromatography as analytical techniques for characterization of the oil fractions from the processing methods will be continued.

LITERATURE SEARCH

A major effort during this report period was a search of the abstract literature to locate relevant articles. The technical literature related to pyrolytic oil covers a broad spectrum. Chemical abstracts were searched from 1948 abstracts to the present time. The keywords used were:

cellulose	pyroligenous acid
char	thermal degradation
gasification	thermolysis
lignin	tar

lignocellulose wood

pyrolysis

The Industrial Arts Index was searched for the period 1950--1957. Starting with 1958, the Industrial Arts Index became the Applied Science and Technology Index, which searched through 1975 under the keyword pyrolysis.

From this search, a large number of references were obtained which are being evaluated for relevance to this investigation. This evaluation will be included in the next report.

A number of books on carbonization, wood chemistry, wood distillation, and related topics that contain useful information and data are as follows:

1. Armstrong, J. 1929. Carbonization Technology and Engineering, C. Griffin Co., London

2. Benson, H. K. 1923. The Chemical Utilization of Wood in Washington. University of Washington, Seattle.

3. Bergstrom, H. 1947. Handbook for Charcoal Burners. Fourth ed. Jernkontoret, Kungstradgardsgaton, Stockholm.

4. Bugge, Gunther. 1925. Die Holzverkohlung und Ihre Erzeugnisse. W. de Gruyter & Company, Berlin

5. Bunbury, H. M. 1923. Destructive Distillation of Wood. D. Van Nostrand Co., New York

6. Dumesny, P. and Noyer, J. 1908. Wood Products: Distillates and Extracts. D. Van Nostrand Co., New York

7. Earl, Derek "Forest Energy and Economic Development" Clarendon Press, Oxford 1975.

8. Hagglund, E. 1951. Chemistry of Wood, Academic Press, New York.

9. Harper, W. B. 1907. The Utilization of Wood Waste by Distillation, Journal of Commerce Co., St. Louis.

10. Hawley, L. F. 1923. Wood Distillation. Chemical Catalog Co., New York.

11. Hawley, L. F. and Wise, L. E. 1926. The Chemistry of Wood. Chemical Catalog Co., New York.

12. Hubbard, E. 1913. The Utilization of Wood Waste. Second ed. Constable & Co., London.

13. Klar, M. 1925. The Technology of Wood Distillation. Chapman & Hall Ltd., London.

14. Stamms, A. J. & Harris, EE Chemical Processing of Wood, Chemical Publishing Company, New York 1953

15. Warner, A. R. Coal Tar Distillation and Working up of Tar Products D. Van Nostrand, New York 1914.

16. Wise, L. E. 1946. Wood Chemistry. Reinhold Pub. Corp., New York.

17. Wise, L. E. & John, E. L. Wood Chemistry 2nd Edition, Reinhold Publishing, New York 1952

In addition, a bibliography on wood distillation was located which contains references starting with 1905. This publication is: Walls, G. A. "Bibliography of Wood Distillation," Oregon State University, Corvallis (966).

SOURCE OF PYROLYTIC OIL

The pyrolytic oil for this study was obtained from the Tech-Air Corporation, which operates a 50 dry ton/day field pyrolysis system

at a lumber yard at Cordele, Georgia. The feed material for this operation is a mixture of sawdust and pine bark. Approximately 110 gallons of oil was obtained on July 15 for use on this project. Oil samples were obtained from the condenser and also from the draft fan. Twenty gallons of the oil is stored in a deep freeze. The physical and chemical properties of the feed material are given in Table I.

TABLE I

Physical and Chemical Properties of

Pine Bark-Sawdust Feed Material

Property	Result	Method
Pinebark	70	Microseparation
Pine sawdust	30	by visual means
Bulk density	21.3 kg./cu.m. 13.3 lbs./cu.ft.	
Moisture	10.3%	ASTM D-1762-64
Ash (by weight)	0.59%	ASTM D-1762-64
Acid Insoluble Ash	<0.01%	
Heating Value (dry basis)	5061 cal./gm. 9109 BTU/lb.	ASTM D-240-64
Elemental Analysis (by weight)		
Carbon	53.3%	
Hydrogen	5.0%	
Nitrogen	0.22%	

CHARACTERIZATION OF PYROLYTIC OIL

Samples of the pyrolytic oil obtained from the Cordele unit were analyzed and the results are given in Table II.

TABLE II

Physical and Chemical Properties of

Pyrolytic Oils from Cordele

Property	Condenser Oil	Draft Fan Oil	Method
Density	1.1415 gm./ml. 9.525 lbs./gal.	1.1075 gm./ml. 9.242 lbs./gal.	-
Water content (by weight)	14.0%	10.4%	ASTM D 95-70
Heating Value (dry basis)	5919 cal./gm. 10,655 BTU/lb.	6563 cal./gm. 11,815 BTU/lb.	ASTM D 240-64
pH	2.9	3.3	Water solution containing 5%
Acid Number	75 mg.KOH/gm.	31 mg.KOH/gm.	ASTM D-664-58
Flash Point	111 °C 233 °F	121 °C 250 °F	ASTM D-93-73
Filterable Solids (by weight)	0.30%	0.4%	Acetone Wash
Copper Strip Corrosion	1	1	Classification-ASTM D-130-7
Sulphur	<0.01%	<0.01%	ASTM D-129-64
Pour Point	26.7 °C 80 °F	26.7 °C 80 °F	ASTM D-97-66

(continued)

Property	Condenser Oil	Draft Fan Oil	Method
Ash (by weight)	0.076%	0.030%	-
Distillation			ASTM D-86
First Drop	98 °C	101 °C	Group 3
10% Point	103 °C	105 °C	
48% Endpoint	NA	265 °C	
53% Endpoint	282 °C	NA	
Solubility (by weight)			
Acetone	99.6%	99.6%	
Methylene Chloride	93.5%	97.8%	
Toluene	Slightly	Slightly	
Hexane	Slightly	Slightly	

Elemental Analysis (% by weight)	Condenser Oil		Draft Fan Oil	
	as received	dry basis	as received	dry basis
Carbon	51.2	59.5	65.6	73.1
Hydrogen	7.6	7.0	7.8	7.4
Nitrogen	0.8	0.9	0.9	1.0

DISTILLATION OF PYROLYTIC OIL

Atmospheric Distillation--A sample of condenser pyrolytic oil, 183 gm., was distilled at atmospheric pressure. Initially, the distillate consisted mainly of water with some oil droplets. Most of the aqueous distillate was obtained over the temperature range of 100°-125°C. Between 125°C and 190°C, the distillate consisted

of mostly oil, which was heavier than water. Starting at 190°C and up to 230°C, the oily distillate contained a phase lighter than water. Some water droplets also distilled over this temperature range. The head temperature began to drop when 110 ml. of distillate had been collected, and the distillation was stopped when the head temperature dropped to 150°C. At this point, the material in the flask has started to smoke. The heavier oily phase was 60% of the total oil distillate, and the lighter oily phase, 40%. Yield data and condition are given in Table III. Data on the oil phases are given in Table IV.

Vacuum Distillation

Condenser oil, 233 gm., was distilled in a simple vacuum distillation apparatus at 0.2-0.4 mm Hg pressure. Dry-ice and liquid nitrogen traps were used to recover the volatile material, including the aqueous phase and light organics. The aqueous phase plus light organics were obtained before the head temperature reached 43°C at which the first oily distillate was obtained. The following fractions were obtained:

Fraction	Head Temperature	% of Total Oil Distillate
1	43°-125° C	44
2	125°-140°C	5
3	140°-180°C	45
4	180°-190°C	6

At 190° head temperature, the material in the flask was becoming more viscous and appeared to be approaching a decomposition stage. The distillation was stopped at this point. Yield data and condition are given in Table III, and data on the combined fractions of the oil are given in Table IV.

TABLE III

Distillation Data

	Atmospheric	Vacuum	Spinning Band Column-Vacuum
Conditions			
Pressure (mmHg)	∿743	0.2-0.4	0.2-0.4
Temperature Range	90°-230°C	43°-190°C	35°-105°C
Fractions of Oil	2	4	9
% Yields			
Aqueous Phase	20.7	23.1	-
Oil Phase	47.5	40.5	59.0
Flask Residue	25.0	32.4	30.0

TABLE IV

Distilled Oil Data

	Atmospheric		Vacuum
	Light Phase	Heavy Phase	
Density, gm/cc	0.9988	1.0423	1.0911
pH	3.5	2.9	2.8
Acid No., mg KOH/gm	17.8	52.0	59.6

VACUUM SPINNING BAND DISTILLATION

A distillation of a sample of the combined oil fractions from the vacuum distillation was carried in a Nester-Faust spinning band distillation column at 0.2-0.4 mm pressure. The following fractions were obtained:

Fraction	Head Temperature	Wt. (gm.)	% of Total Oil Spilled
1	35-48	3.28	13.5
2	48-58	5.97	24.5
3	58-60	3.48	14.2
4	60-68	0.87	3.6
5	68-74	2.81	11.5
6	74-82	2.47	10.2
7	82-88	1.89	7.8
8	88-98	1.13	5.4
9	98-105	2.26	9.3
Flask Residue	-	12.3	-

The flask residue, 30% of the total charge, was a black tarry material. The trap contained 3.2 g. of material, and some material remaining in the column. The percent recovery of the oil fractions, trap material and flask residue was 96.7%.

CHEMICAL AND PHYSICAL CHARACTERIZATION

The results on the characterization of the pinebark-sawdust feed material and of the Cordele pyrolytic oils are given in Tables I and II along with the analytical methods used. In addition to these analytical methods, laboratory work is underway to determine the feasibility of utilizing liquid and/or gas chromatography as a means of obtaining data on the original pyrolytic oils and fractions of oil from different processing techniques. The data should be useful in assessing the effects and value of different processing techniques on the pyrolytic oil. Other analytical techniques will be utilized as needed for evaluation of different oil fractions.

TECHNICAL PAPER

A technical paper, "Pyrolysis of Pine Sawdust," was presented at the "Symposium on Thermal Properties, Pyrolytic Conversion and Combustion of Carbohydrates and Lignins" of the national meeting of the American Chemical Society, San Francisco, Aug. 29-Sept. 3, 1976. See Appendix A.

EXPENDITURES

The expenditures through August 31, 1976 and estimated expenditures for September 1976 are as follows:

a)	Expenditures through August 31, 1976	
	Personal Services	$3,992.17
	Retirement 9.1%	363.29
	Material & Supplies	303.13
	Travel	8.00
	Overhead 68%	2,714.68
	Total	$7,381.27
b)	Estimated expenditures for September 1976	
	Personal Services	$2,969.00
	Retirement 9.1%	270.00
	Travel	250.00
	Material and Supplies	250.00
	Overhead	2,019.00
	Total	$5,758.00
c)	Total budget	$65,000.00
	Expenditures, First Quarter	13,139.27
	Remaining Funds	$51,860.73

Appendix A

PYROLYSIS OF PINE SAWDUST

J. A. Knight

Presented
at
SYMPOSIUM ON THERMAL PROPERTIES,
PYROLYTIC CONVERSION AND
COMBUSTION OF CARBOHYDRATES AND LIGNINS

- - -

American Chemical Society
National Meeting
San Francisco

August 29, 1976
through
September 3, 1976

PYROLYSIS OF PINE SAWDUST*

J. A. Knight

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

INTRODUCTION

The utilization of waste materials is of vital concern in the United States because these materials--agricultural, forestry and municipal wastes--represent unused resources and in many cases present serious disposal problems. During the past several years, a great deal of attention has been given to pyrolysis as a means of converting these materials into useful products, particularly fuels. Workers at the Engineering Experiment Station (EES), Georgia Institute of Technology, have been utilizing the pyrolysis approach to convert agricultural and forestry wastes into char, pyrolytic oil and combustible gases.[1,2,3] Particular attention is being given to forestry wastes at the EES. Forestry wastes represent a relatively homogeneous material, are generated widely throughout the U.S. in abundance the year round, and represent a renewable resource. In many cases they are generated in large concentrated quantities at sites such as sawmills and paper mills. In the U.S., it has been estimated that 100 million dry tons/year of forestry wastes are generated annually.[4]

Work with forestry wastes at the EES has been mainly with pine bark and sawdust because of its importance to the southeastern states. The EES has two continuous pyrolysis pilot plants which are used in research and development work in the pyrolysis of all types of lignocellulosic materials and municipal refuse. One of the pilot plants will process 1,500 pounds of dry feed per hour, and the other system will process 800 pounds of dry feed per hour. The experiments

*Supported in part by EPA Grant No. R 804416010.

reported in this paper on the pyrolysis of sawdust in a tube furnace were conducted to provide data mainly on the yields of products, the heating values of the products, and composition of noncondensible gases over the temperature range of 540°C to 870°C. From these data, heat and mass balances were determined. These data are useful as guidelines in the operation of the two continuous pilot plant systems.

EXPERIMENTAL

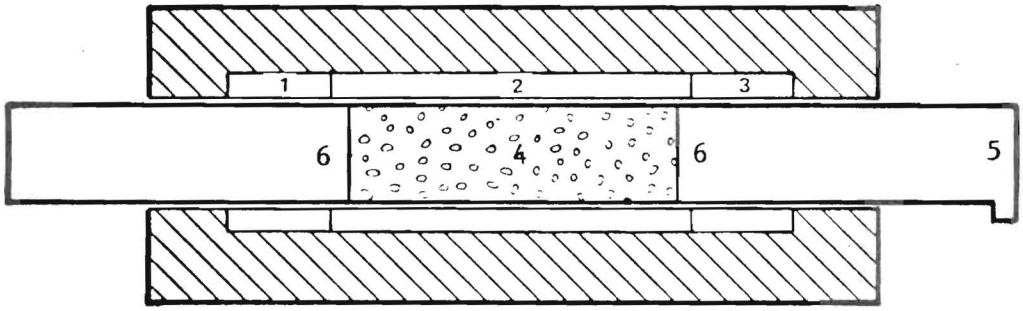
Feed Material - The feed material was pine sawdust and was dried to 6 percent moisture on a wet basis. The sawdust on a dry basis had 1.2 percent total ash, 0.3 acid insoluble ash, and a heating value of 8103 BTU/lb. The bulk density of the sawdust was 14.1 lbs./cu. ft., and 20% was +4 mesh; 68.0%, 4 x 16; 10.4%, 16 x 35; and the remainder, 1.6%, less than 35 mesh.

Pyrolysis - The pyrolysis experiments were conducted in a Lindberg Hevi-duty, six inch tube furnace, Figure 1, fitted with a stainless steel tube (type 306). The furnace has three sections which can be heated independently. Thermocouples were placed in the charge and the exit gas space. A charge of 2500 grams of sawdust, 6% moisture on a wet basis, was held in place in the center of the tube with spacers. The furnace was heated until the evolution of gases had essentially ceased. The temperatures of the furnace, in the center of the charge and at the gaseous exit, are given in Table 1.

TABLE 1

MAXIMUM TEMPERATURES DURING PYROLYSIS

Location	Degrees C			
Furnace	540°	650°	760°	870°
Middle of Charge	500°	610°	700°-740°	720°-810°
Gaseous Exit	230°	280°	320°	360°



1. Furnace Thermocouple
2. Furnace Thermocouple
3. Furnace Thermocouple
4. Thermocouple in center of charge
5. Thermocouple at gaseous exit
6. Spacers

Lindberg Hevi-Duty Furnace

Figure 1

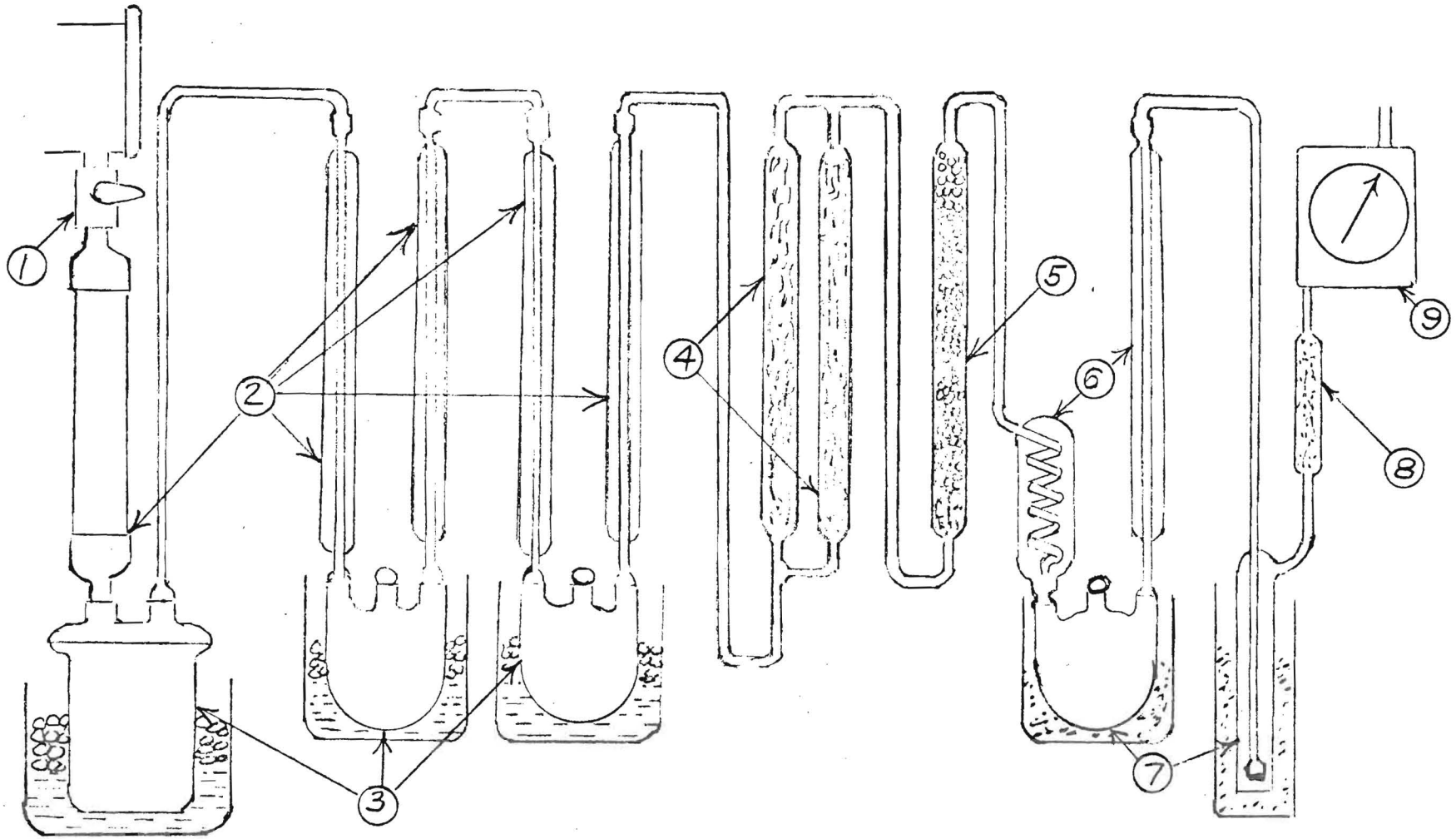
The temperature at the exit end of the tube was high enough so that condensation did not occur. The gas evolution rate for each experiment showed a rapid increase when the center of the charge reached the 150°C-175°C range and continued to evolve at a fairly rapid rate until the maximum temperature was reached. The off-gases were passed through a condensation train, Figure 2, so as to condense the organic and aqueous material, and the gases were collected in large plastic gas collection bags. Total volume of evolved gases were measured with a dry test meter.

At the end of a pyrolysis experiment, the ball valve, Figure 2, was closed, and the char, after cooling to room temperature, was removed, weighed and samples prepared for analysis.

Condensation Train and Collection of Organic and Aqueous Phases - The off-gases from the pyrolysis tube pass through a stainless steel ball valve (1)* and then through a series of water cooled condensers (2) and ice cooled traps (3) (See Figure 2). A jacketed stainless steel tube is used for the first condenser in place of a glass condenser. The use of a resin kettle as the first trap facilitates the recovery of viscous, oily condensates. The gas stream then passes through the two parallel glass-wool demisters (4) and a calcium sulfate ("Drierite") column (5) into a series of cold condensers (6) and cold traps (7). The purpose of the demisters is to remove oil mist, and the calcium sulfate is used to remove the last traces of moisture from the stream. The cold condensers (6) are chilled with ethanol, which circulates through a heat exchanger coil immersed in dry ice and acetone, and the traps (7) are immersed in a bath of dry ice and acetone. From the cold traps the

*The number in parenthesis refers to the number in Figure 2.

2. Water cooled condensers
3. Ice cooled traps
4. Glass wool demisters
5. Drierite column
6. Cold condensers
7. Dry-ice traps
8. Magnesium perchlorate drier
9. Dry test meter



Condensation Train

Figure 2

gases pass through a magnesium perchlorate drier (8) and a calibrated dry test meter (9) into a series of 96 liter gas collection bags. The use of magnesium perchlorate has been found to prevent fouling of gas chromatographic columns during analysis of the noncondensible gases. The quantity of magnesium perchlorate is held to a minimum, and precautions are taken to prevent any explosion hazard. At the completion of an experiment, the weights of the condensates were stored in tightly closed containers. Heavy organic and aqueous condensates were stored at ambient temperature and the condensates from the dry ice traps were stored in a freezer.

Noncondensed Gases - During the pyrolysis experiment, the gases were collected in 90 liter quantities successively in 96 liter gas collection bags. After each bag is filled, it was kneaded to mix its contents, and approximately half of its contents were aspirated through gas collection tubes (~ 250 ml capacity). Two gas collection tube samples were taken for analysis.

Analytical Procedures

Heating Values - The heats of combustion of the feed material, chars and organic liquids were determined in a Parr bomb calorimeter using the ASTMD-240-64 method.

Water in Pyrolytic Oils and Aqueous Phases - The percent water in the pyrolytic oil phases and aqueous phases was determined by a two hour distillation with toluene in a Dean-Stark apparatus. The percent water in the pyrolytic oils was generally less than 25%, and the percent water in the aqueous phase was generally greater than 75%. The ASTMD-95-70 method (modified) was followed in these determinations.

Volatiles in Char (Low Temperature) - The weight loss in the char was determined by drying a weighed sample for two hours at 105°C followed by cooling one hour in a vacuum desiccator.

Volatiles in Char (High Temperature) - The volatiles in a char sample were determined by heating the sample in a covered porcelain crucible from the 105°C determination at successive temperatures sequentially in three muffle furnaces as follows: 2 minutes at 300°C; 3 minutes at 500°C, and 6 minutes at 900°C. The sample was cooled in a vaccum desiccator and then weighed to determine weight loss, which was calculated as % volatiles. This procedure is an adaptation of ASTM 1762-64 method.

Total Ash - The char sample from the volatiles determination was ignited without the crucible cover to constant weight at 550-600°C, cooled to room temperature and weighed.

Gas Analysis - The gases were analyzed utilizing four gas chromatographic units, and the conditions are given in Table 2.

TABLE 2

GAS CHROMATOGRAPHIC ANALYTICAL CONDITIONS

Gas Component	G.C. Column	Temp	Flow Rate, Carrier Gas	Detector and Instrument
Hydrogen	Silica gel; 60 x 80 mesh, 6' x 1/8"	32°C	18 ml/min; Argon	Thermal Conductivity; Carle AGC
Oxygen, nitrogen methane, carbon monoxide	Molecular sieve, 13 x; 60 x 80 mesh, 12' x 1/8"	40°C	20 ml/min; Helium	Thermal Conductivity; Perkin Elmer 990
Carbon dioxide	Activated carbon; 60 x 80 mexh, 10' x 1/8"	150°C	22 ml/min; Helium	Thermal Conductivity; Carle AGC
Hydrocarbons C_2-C_5's	Alumina F-1; 60/80 mesh,	50°-150°C at 12°/min.	24 ml/min; Nitrogen	FID; Perkin Elmer 800

RESULTS AND DISCUSSION

The yields of the four major pyrolytic products versus temperature are presented in Figure 3. The char yield decreases with increasing temperature and levels out at about 760°C. The yield of the combined oil condensates does not show any noticeable change with temperatures, except for the value at 760°. This higher value may be due, in part, to an experimental error. The yield of the combined noncondensible gases increases with temperature and the water yield decreases with temperature. The sums of the yields of all the products are within experimental error and show that essentially all of the products were recovered.

Analysis of the noncondensible gases showed that major gases are hydrogen, methane, carbon monoxide, and carbon dioxide. The C_2, C_3 and C_4 hydrocarbons are produced in relatively small amounts, and no experimental attempt was made to identify the individual components of these hydrocarbons. The variations of the yields of these gases are shown in Figure 4. The carbon monoxide and carbon dioxide both show significant decreases in yield with increasing pyrolysis temperature. The hydrogen yield shows a dramatic increase for the temperature range investigated. The methane yield increases to a maximum at approximately 680°C and then shows a gradual decrease at the higher temperatures. Based on the gas composition, heating values of the gaseous mixture produced at each temperature were calculated, and these are presented in Figure 5.

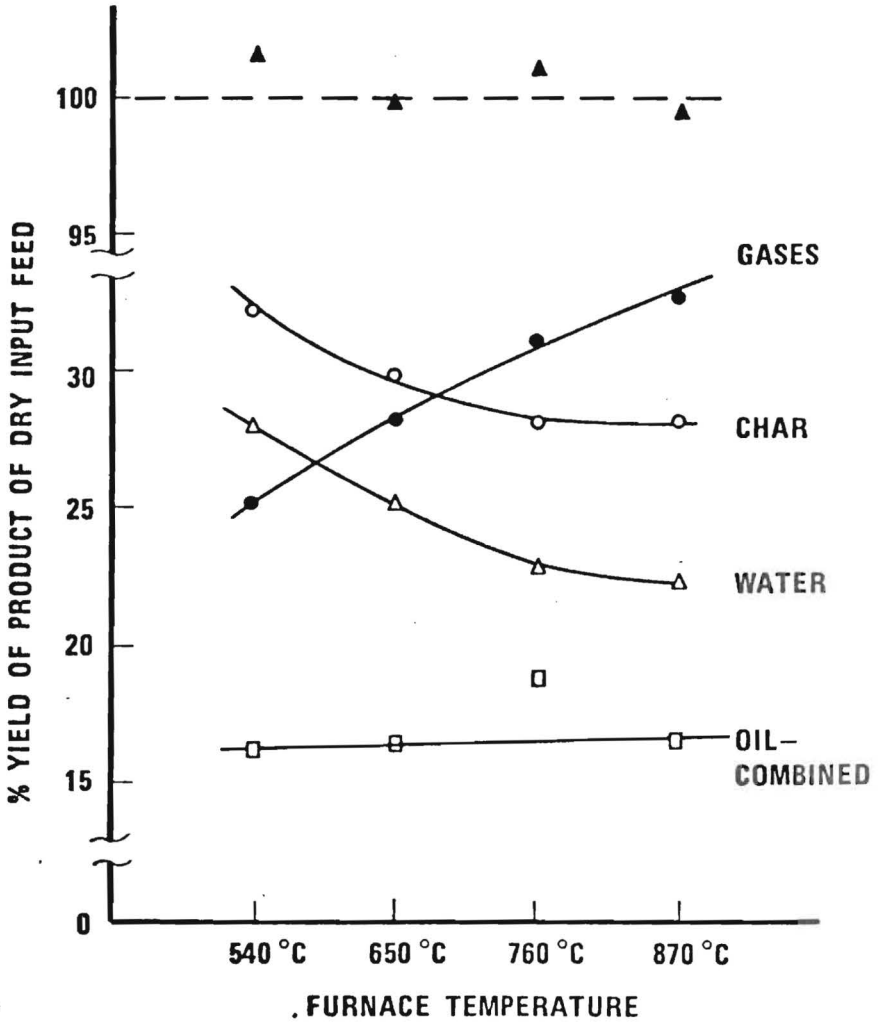

100
95
30
25
20
15
0
% YIELD OF PRODUCT OF DRY INPUT FEED
GASES
CHAR
WATER
OIL–
COMBINED
540 °C
650 °C
760 °C
870 °C
FURNACE TEMPERATURE

Figure 3

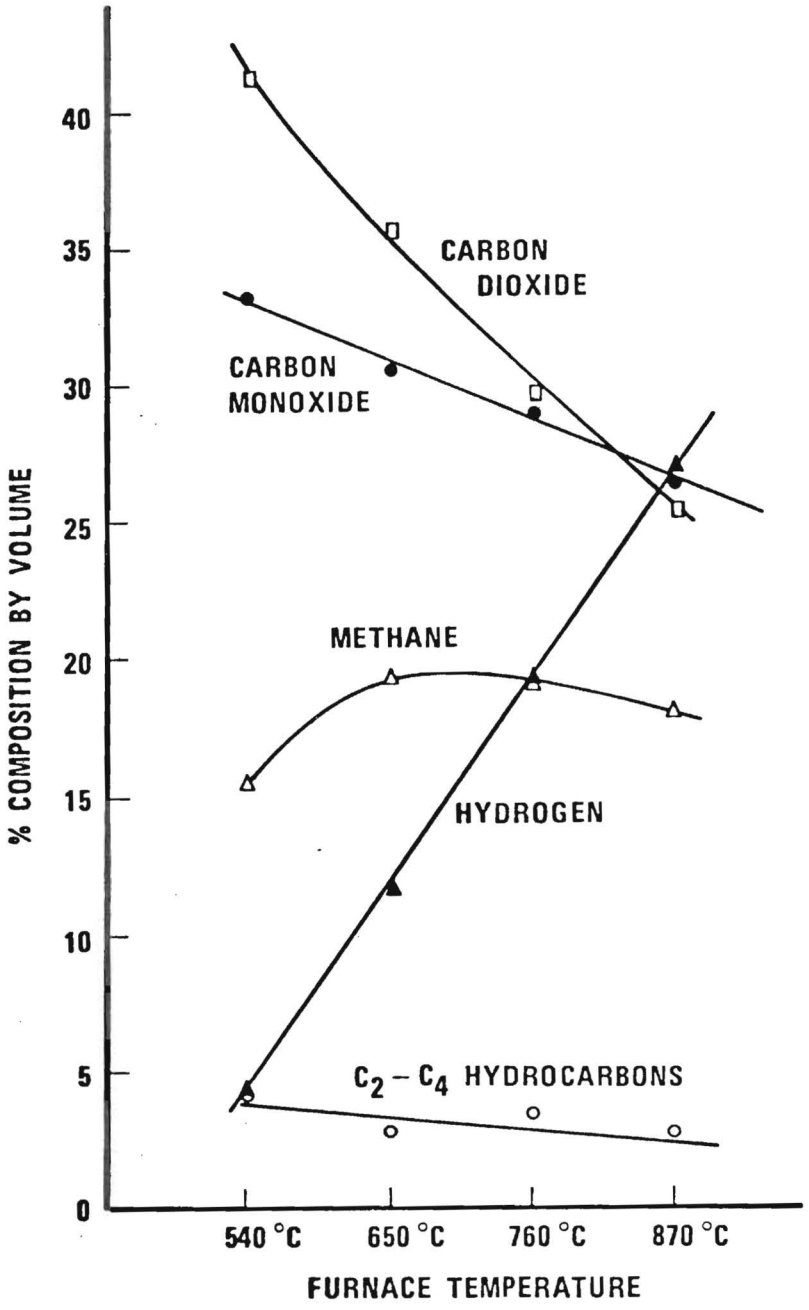

% COMPOSITION BY VOLUME
40
35
30
25
20
15
10
5
0
CARBON DIOXIDE
CARBON MONOXIDE
METHANE
HYDROGEN
$C_2 - C_4$ HYDROCARBONS
540 °C
650 °C
760 °C
870 °C
FURNACE TEMPERATURE

Figure 4

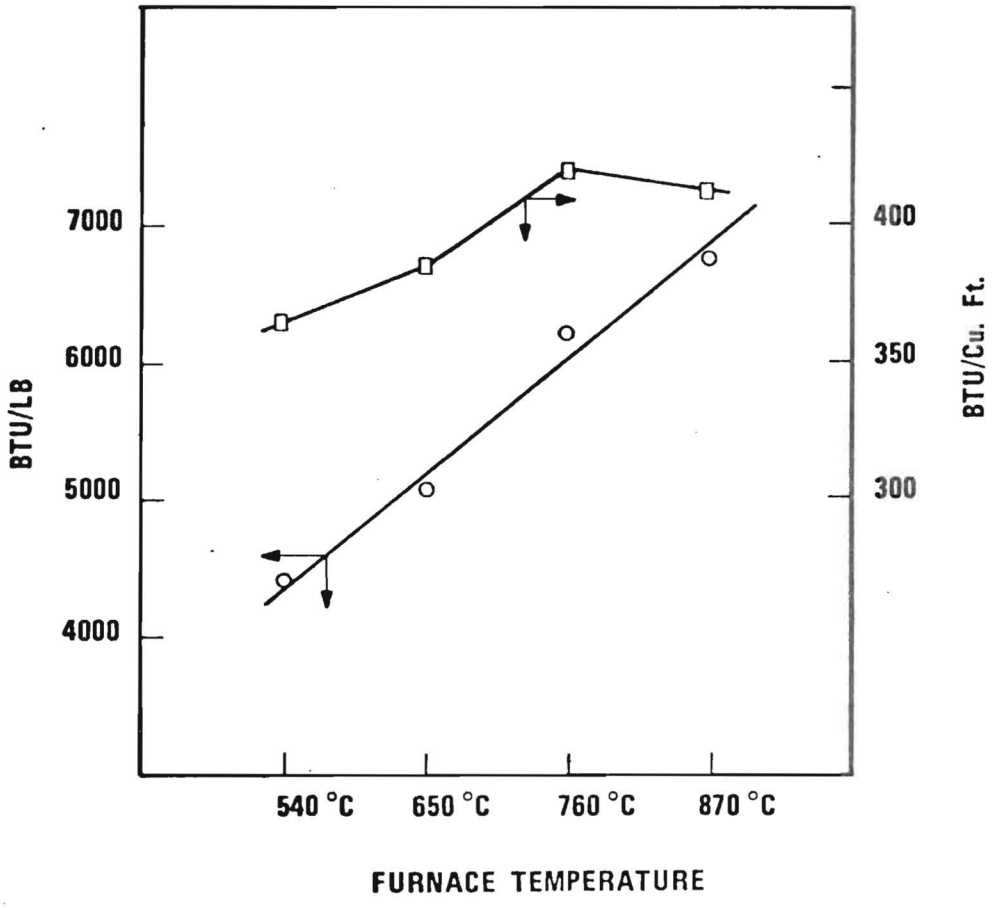

7000
6000
5000
4000
BTU/LB
400
350
300
BTU/Cu. Ft.
540 °C
650 °C
760 °C
870 °C
FURNACE TEMPERATURE

Figure 5

The heating values of the pyrolytic gas which range from 365 to 420 BTU/cu. ft., increases with increasing temperature to 760°C and then decrease slightly. In actual practice in a continuous pyrolysis system, the heating value of the gas will be decreased by nitrogen from process air.

The pyrolytic oil from the off-gas stream was collected into three different samples from the condensation train. The yields of each of these oils are presented in Figure 6, along with the combined yield. The reason for the higher yield values obtained for condensates #1 and #2 at 760°C is not known. It is felt that they may be attributed in part to experimental error. This oil condensate #1 obtained from the first condenser represents the largest fraction and shows that the oil yield decreases as the temperature decreases. The oil condensate #2 obtained from the next two condensers shows a slight increase with increasing temperature. The oil yield represented by the "Cold Trap" was condensed from the stream in a dry ice trap and was a relatively volatile material. In actual practice in a continuous pilot plant operation, this oil would not be condensed from the off gas stream and would add to the heating value of the gas. The heating values of the oils are given in Table 3 and are in the 12,000 to 14,000 BTU/lb. range on a dry basis. In the operation of our continuous pilot plant pyrolysis units, the general practice is to operate the condenser so that the pyrolytic oil does not have more than 15% water. The remaining noncondensed gases, including water vapor, are burned in the after-burner.

The heating values of the pyrolytic products obtained at each temperature are given in Table 3. In Figure 7, the heat available from each product versus temperature is presented. The significant information to be gained from this graph is that the sum of the heats available from each product

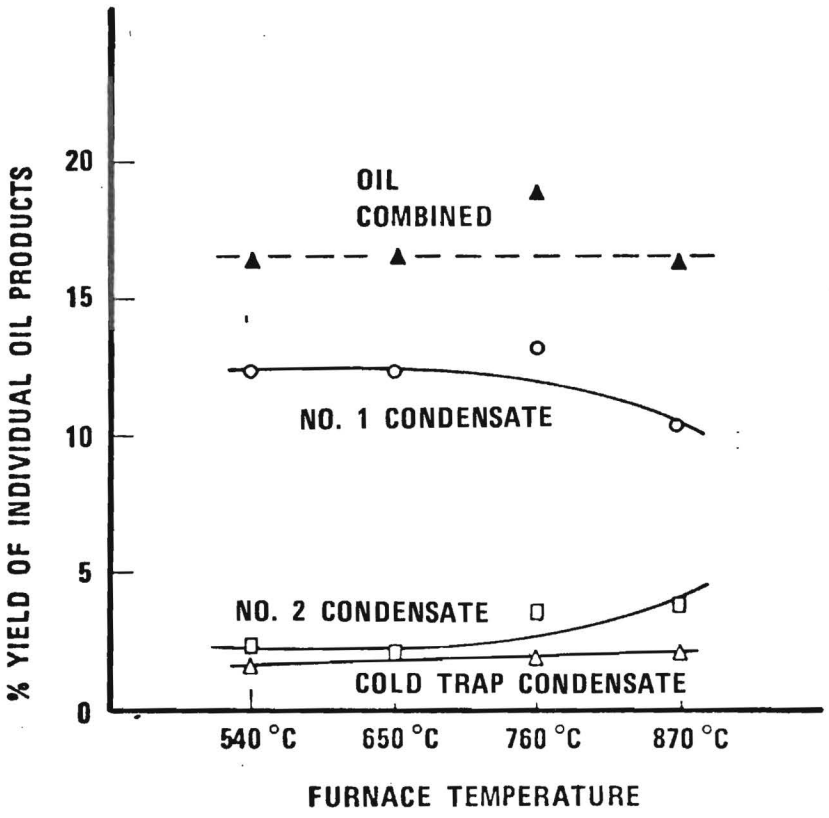

% YIELD OF INDIVIDUAL OIL PRODUCTS
20
15
10
5
0
OIL
COMBINED
NO. 1 CONDENSATE
NO. 2 CONDENSATE
COLD TRAP CONDENSATE
540 °C
650 °C
760 °C
870 °C
FURNACE TEMPERATURE

Figure 6

TABLE 3

HEATING VALUES OF PYROLYTIC PRODUCTS

	Furnace Temperature			
Product	540°C	650°C	760°C	870°C
Gas, BTU/lb.	4,407	5,029	6,193	6,777
Gas, BTU/Cu.ft.	365	384	420	412
Oil, First Condensate BTU/lb	13,529	14,072	13,153	14,004
Oil, Second Condensate BTU/lb	12,158	13,555	12,637	12,716
Oil, Dry Ice Condensate BTU/lb	13,362	13,643	13,290	13,432
Char, BTU/lb.	14,357	14,441	14,218	14,053

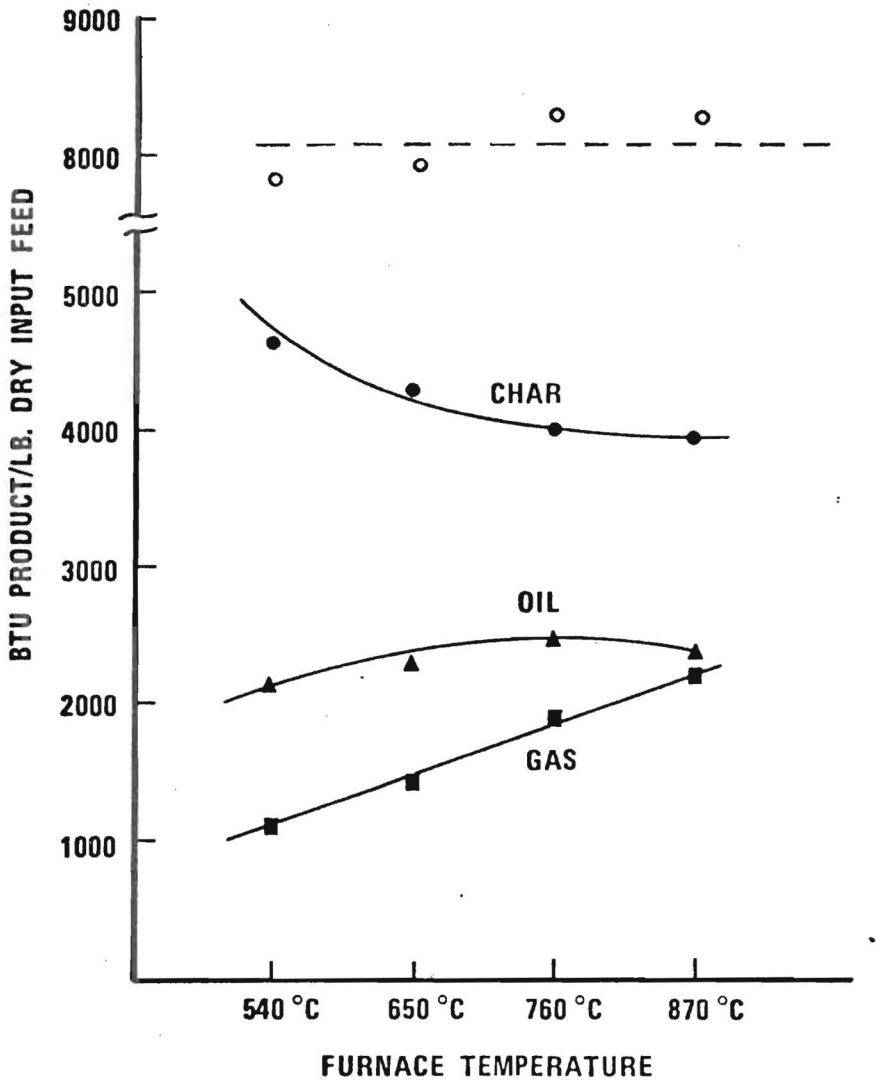

9000
8000
5000
4000
3000
2000
1000
BTU PRODUCT/LB. DRY INPUT FEED
CHAR
OIL
GAS
540 °C
650 °C
760 °C
870 °C
FURNACE TEMPERATURE

Figure 7

at each pyrolysis temperature is very close to the heat content of the dry input feed material. These data show that the total heat content of the input material is available for use in the three fuels--char, oil, and gas--that are produced in the pyrolysis process. In Figure 8, the percent recovery of each of the pyrolytic products of the input feed is presented. These data show that the heat values in the char and oil decrease with increasing temperature with more gas being produced. At 540°C, for example, the char and first oil condensate represent 77.5% of the total heat value of the input feed, whereas at 870°C, they represent 66.7%. In order to obtain the maximum recovery of the heat content of the products, the gases must be utilized on site. A portion of the gases can be used for drying input feed as the process operates best using feed material of less than 10 percent moisture.

Additional analytical data on the char samples is presented in Table 4. The significant information from this table is the total volatiles in the char. The data show the temperatures that the char must be subjected to in order to produce a char with a particular volatile content.

In summary, these bench scale pyrolysis experiments over the temperature range 540°C to 870°C provide data on the yields of the pyrolytic products, the composition of the gaseous phase, the heating values of the products, and the heat and mass recovery in the different products.

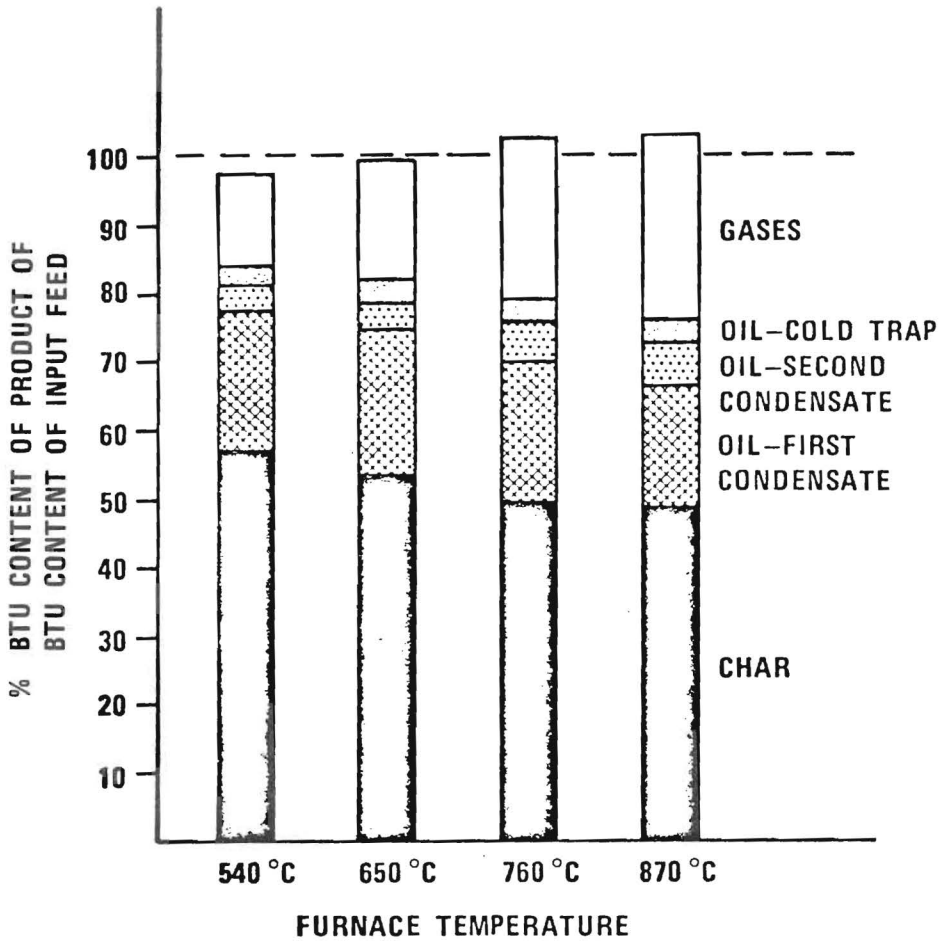

% BTU CONTENT OF PRODUCT OF
BTU CONTENT OF INPUT FEED
100
90
80
70
60
50
40
30
20
10
GASES
OIL–COLD TRAP
OIL–SECOND
CONDENSATE
OIL–FIRST
CONDENSATE
CHAR
540 °C
650 °C
760 °C
870 °C
FURNACE TEMPERATURE

Figure 8

TABLE 4

CHAR ANALYTICAL DATA

	Furnace Temperature			
	540°C	650°C	760°C	870°C
Weight Loss at 105°C (2 hr.),* %	1.1	0.5	0.6	1.0
Total ash, %	2.3	4.6	3.6	3.9
Volatiles, %	13.7	7.1	3.7	2.8

*Weight loss probably due to vapors adsorped during cooling of char after pyrolysis.

REFERENCES

1. J. A. Knight, et al, "Pyrolytic Conversion of Agricultural Wastes to Fuels," Presented at 1974 Annual Meeting of American Society of Agricultural Engineers, Oklahoma State University, Stillwater, Oklahoma, June 23-26, 1974.

2. J. A. Knight and M. D. Bowen, "Pyrolysis--A Method for Conversion of Forestry Wastes to Useful Fuels," Presented at Southeastern Technical Division of American Pulpwood Association, Atlanta, Georgia, Nov. 5-6, 1975.

3. J. A. Knight and M. D. Bowen, "Pyrolysis--A Method for Conversion of Forestry Wastes to Useful Fuels," Presented at Workshop on Wood Residues: An Alternate Energy Source for New England Industry, University of New Hampshire, Durham, New Hampshire, April 7-8, 1976.

4. Heyward Taylor, Division of Engineering, Forest Service, U. S. Dept. of Agriculture, Private Communication.

B-469

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

Atlanta, Georgia

Quarterly Report No. 2

October 1, 1976--January 31, 1977

Project B-469

UTILIZATION AND/OR STABILIZATION OF PYROLYTIC OIL FROM PYROLYSIS OF AGRICULTURAL, MUNICIPAL AND OTHER WASTES

by

J. A. Knight

Grant No. R 804 416 010

Performed for

Municipal Environmental Research Laboratory

Environmental Protection Agency

Cincinnati, Ohio 45268

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PROJECT B-469

Utilization and/or Stablization of Pyrolytic Oil from Pyrolysis of Agricultural, Municipal and Other Wastes

Report Period October 1, 1976 - January 30, 1977

SUMMARY

The technical references obtained in the literature search have been organized and a bibliography prepared, which is given in Appendix A. The work with the literature is continuing so that an excellent technical literature base can be established on the pyrolysis of lignocellulosic and carbonaceous materials for maximum resource recovery with particular emphasis on pyrolytic oil.

The technical paper, "Pyrolysis of Pine Sawdust," was presented at the Symposium on Thermal Properties, Pyrolytic Conversion and Combustion of Carbohydrates and Lignins, August 29--September 3, 1976, American Chemical Society, San Francisco. This symposium has been published by Academic Press and is entitled "Thermal Uses and Properties of Carbohydrates and Lignins," edited by Fred Shafizadeh, Kyosti V. Sarkanan and David A. Tillman. A copy of the reprint is appended in Appendix B.

The distillation experimental program has been continued with steam distillation and vacuum removal of the water from the pyrolytic oil. Steam distillation of the raw condenser oil was carried out to determine what quantity of organic material could be separated effectively by this technique. Only a small amount of organic material (approximately 2% or less) was obtained in this manner with steam alone. Larger quantities of organic material are obtained with additional heating of the flask containing the oil. An effective means for removal of the water from the raw pyrolytic oil is vacuum stripping of the raw oil.

Considerable effort has been expended in developing analytical techniques, particularly liquid chromatographic methods, which can be used effectively in

"fingerprinting" the oil so that different processing methods can be followed and the products characterized relative to the raw oil. The liquid chromatographic conditions that have been found most suitable to date utilize a Partisil ODS 5μ column and a solvent system of acetonitrile and water. Molecular weight distributions, utilizing size exclusion chromatography, were obtained for selected samples of oils and fractions of oil.

Other analytical determinations include elemental analyses, heating values, acidity and viscosity on selected samples of oil and fractions obtained from the different distillation experiments.

WORK PROGRAM FOR NEXT REPORT PERIOD

The following work program is planned for the next reporting period, February through May, 1977:

The current literature search work will be continued with emphasis on evaluation and summarization of the literature so as to provide an excellent technical literature base with relevance to pyrolysis and resource recovery from lignocellulosic and carbonaceous materials.

The results of the distillation experiments will be evaluated and additional data on the fractions will be obtained, if needed. Based on the results of these evaluations, additional distillation experiments will be planned and carried out, if warranted, so as to provide the necessary data base to evaluate distillation techniques for processing raw pyrolytic oil.

Preliminary experimental column chromatography and extractive experiments with the raw oil will be carried out to determine if these are effective techniques for separating the oil into more chemically homogenous fractions.

The experimental work with the analytical techniques particularly liquid and gas chromatography will be continued.

LITERATURE SEARCH

The references from the technical literature search have been arranged according to year of publication, and this list is given in Appendix A. The literature work is continuing with continued searching of current literature

and evaluation of literature. The ojbective of the literature work is to establish an excellant technical literature base on the pyrolysis of lignocellulosic and carbonaceous materials, which can be used for planning and establishing experimental programs for the investigation of the pyrolysis of lignocellulosic and carbonaceous materials and of the pyrolytic products.

EXPERIMENTAL WORK

Distillation

On the first quarterly report, the work on the atmospheric, simple vacuum and fractional vacuum distillation was reported. The work has been continued this quarter with steam distillation and vacuum stripping the pyrolytic oil primarily with the objective of removing the water.

Steam Distillation

Two steam distillations were carried out with the raw condenser oil. In the first steam distillation, 8.8 g. of an oily layer plus 385 g. of a water layer was collected with steam only at a temperature up to 105°C. At this point heat was applied to the flask in addition to steam injection. The distillation was continued with the temperature rising to 190°C. The data on the quantities of distillates and residue are given below. An initial charge of 1,238 gm. of condenser oil (14.03% water) was used in this experiment.

Steam Distillation One

Temperature Range	Up to 105°C	105° - 150°C	150° - 190°C
1. Aqueous Phase	385 gm.	420 gm.	279 gm.
Water	354 gm.	359 gm.	228 gm.
Organic	31 gm.	61 gm.	51 gm.
2. Organic Phase	8.8 gm.	33.8 gm.	183 gm.
3. Residue (organic)	-	-	468 gm.

Total organic material recovered = 836.6 gm.
% Recovery of organic based on raw oil on dry basis = 78.6 %

In the second steam distillation, essentially the same procedure was used except that the flask after the initial steam distillate was collected was only

heated to maximum temperature of 160°C. The data from this distillation are given below. An initial charge of 549 gm. of condenser oil (14.03% water) was used in this experiment.

Steam Distillation Two

Temperature Range	Up to 108°C	108-160°C
1. Aqueous Phase	383 gm.	254 gm.
Water	365 gm.	229 gm.
Organic	18 gm.	25 gm.
2. Organic Phase	7.3 gm.	14.2 gm.
3. Residue	-	361 gm.
Water		12 gm.
Organic		349 gm.

Total organic material recovered = 413.5 gm.
% Recover based on raw oil on dry basis = 87.6%

Vacuum Stripping of Water from Raw Pyrolytic Oil

Two experiments were carried out under vacuum for the removal of water from the pyrolytic oils. In each experiment, a pressure of 0.3 mm. of mercury was maintained and dry ice-acetone and liquid nitrogen traps were used to collect the volatile organic and aqueous fractions. In the first experiment, the flask temperature was raised to 55°C, and in the second experiment, the flask temperature was maintained at 25°C. The data from these experiments are given below.

Vacuum Stripping of Water from Pyrolytic Oil

	Weight %	
	Experiment 1	Experiment 2
	Up to 55°C	25°C
Aqueous Phase		12.9
Water	12.4	
Organics	4.4	
Organic Phase	0.35	1.3
"Dried" Oil	82.36	84.32
Total	99.51	98.52

Liquid Chromatographic Procedures

The pyrolytic oils are heat sensitive and reactive and contain a relatively large number of organic compounds. An analytical technique was needed which could be used in analyzing the fractions of oil obtained by the different processing methods that would not change the chemical character of the fractions. Liquid chramotography (L.C.) appears to be the method of choice because liquid chromatography is carried out at ambient temperature, is capable of high resolution of complex mixtures, and the component detection is nondestructive. In addition, the pyrolytic oils are soluble in organic solvents-aqueous systems which are useful in L.C. The main initial objective of utilizing L.C. in the pyrolytic oil work is to provide a method to obtain a "fingerprints" of the raw oil and fractions obtained from it for comparsion and correlation.

L.C. Column Testing

In order to select the most suitable L.C. column, several columns were tested with the raw pyrolytic oil using a one ml./min. flow rate and detector at 254 nm. The chromatographic columns and conditions tested and the results are given below in order in which the testing was carried out.

A. Vydac adsorption silica gel 30μ column. Solvent, 0-100% isopropanol (IPA) in isooctane, 20 min. gradient 20 concave.* Results: No resolution obtained; only one large peak.

B. Partisil adsoprtion silica gel 5μ column. Solvent, 5-30% IPA in isooctane 20 min. gradient, linear. Results: Resolution at only eight peaks.

C. Partisil PAC 5μ column. Solvent, 0-100% IPA in isooctane, 30 min. gradient 35 concave. Results: Resolution of 12 to 20 peaks. See Figure 1.

D. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in H_2O, 30 min. gradient 35 concave. Results: Resolution of 30-40 peaks. See Figure 2.

E. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in H_2O, 10 to 40% with 20 minute hold then 40% to 100% 35 concave gradient. Results: Resolution of 46-50 peaks. Total run time 60 minutes. See Figure 3.

*Term used as a dial setting for Logarithmic slope control on Micrometritic L.C. models only.

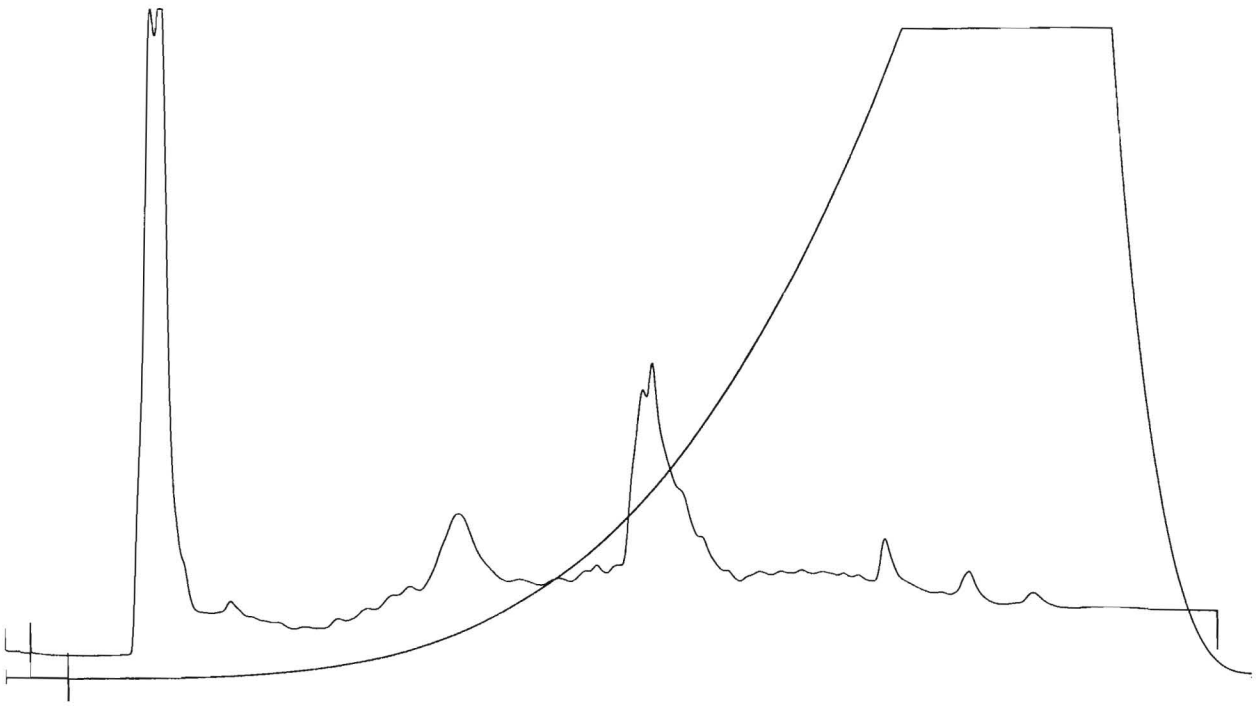

Figure 1. Liquid Chromatogram Partisil PAC Column, 0-100% Gradient of IPA in Isoctane.

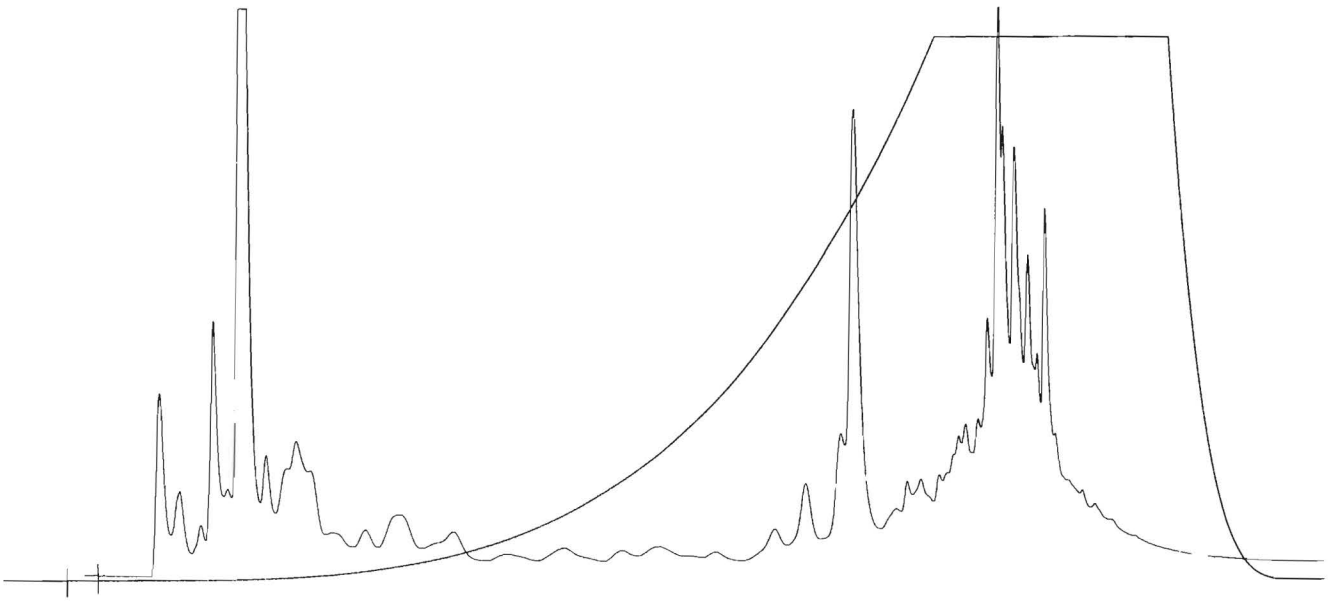

Figure 2. Liquid Chromatogram Partisil ODS, 10-100% Gradient of Acetonitrile in Water.

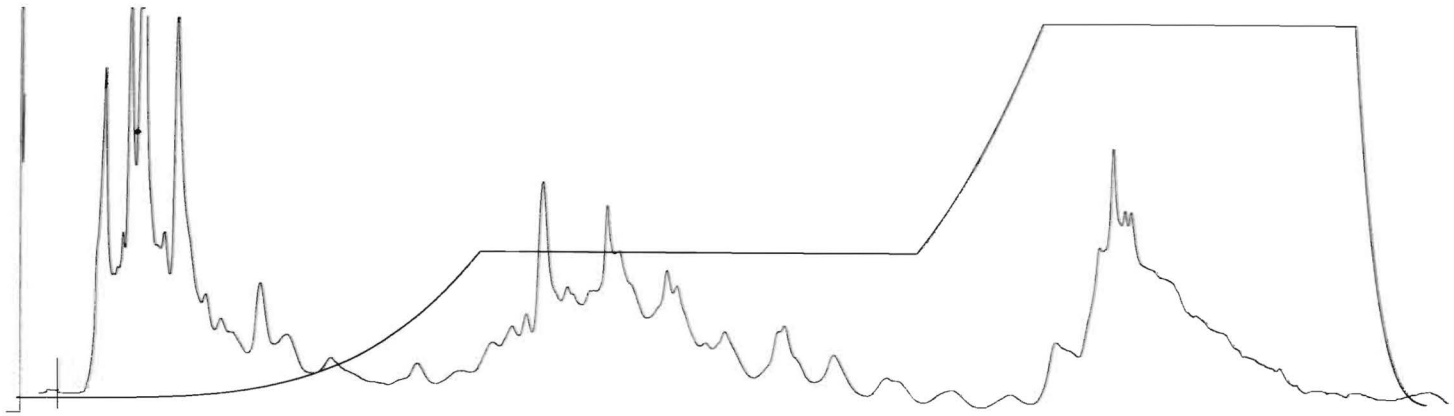

Figure 3. Liquid Chromatogram Partisil ODS, 10-40% hold 20 min. the 40% to 100% Gradient.

From the above results, the resolution obtained with the column and conditions given in E above appeared to be very suitable for our purposes.

Testing of Other L.C. Variables

In arriving at the conditions given in E the other variables tested were wavelength, solvent gradient, and fow rate. The testing and results of these variables are given below.

A. Wavelength

Wavelengths 200, 220, 254, 280, 300, 320, 360 nm. were chosen, and L.C. runs were made using constant conditions (E above) other than wavelength. Results: It was noted that many compound responses appeared or disappeared with the change in wavelength. No one wavelength was entirely satisfactory because at shortest wavelengths of 200-220 nm. excessive peak blending occurred with high background levels which gave poorer peak resolution. The lower wavelength of 300-360 nm. produced sharply resolved peaks, but only a small total number of peaks actually appeared. Best results for our purposes were obtained at 280 nm. with 254 nm. being the alternative choice. See Figures 4 through 8 for liquid chromatograms.

B. Solvent Gradient

1. A 10-100% acentonitrile 35 concave 30 min. long run with no holds produced a short, fairly well resolved chromatogram with crowding of peaks only at the last 25% of the run. See Figure 2.
2. A 10-40% acetonitrile in water 35 concave and hold for 20 min., then to 100% for 10 min. produced a very well resolved chromatogram in a total of 60 min. This run produces typically 50 discernable peaks from the raw condenser oil test sample. See Figure 3.
3. A gradient with 5 min. holds at 20%, 30%, 40%, then 10 min. at 100% did not produce a better resolved chromatogram

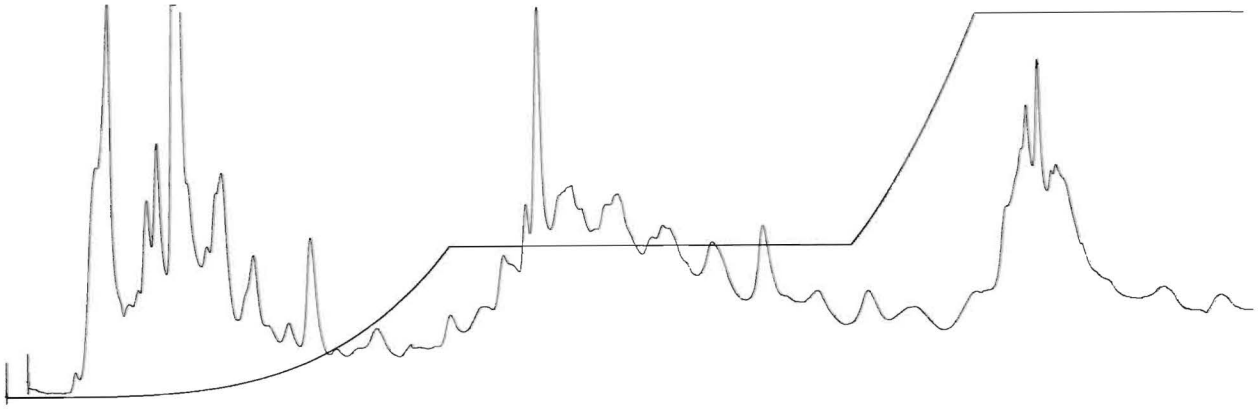

Figure 4. Liquid Chromatogram Partisil ODS, 210 nm. Detector Wavelength.

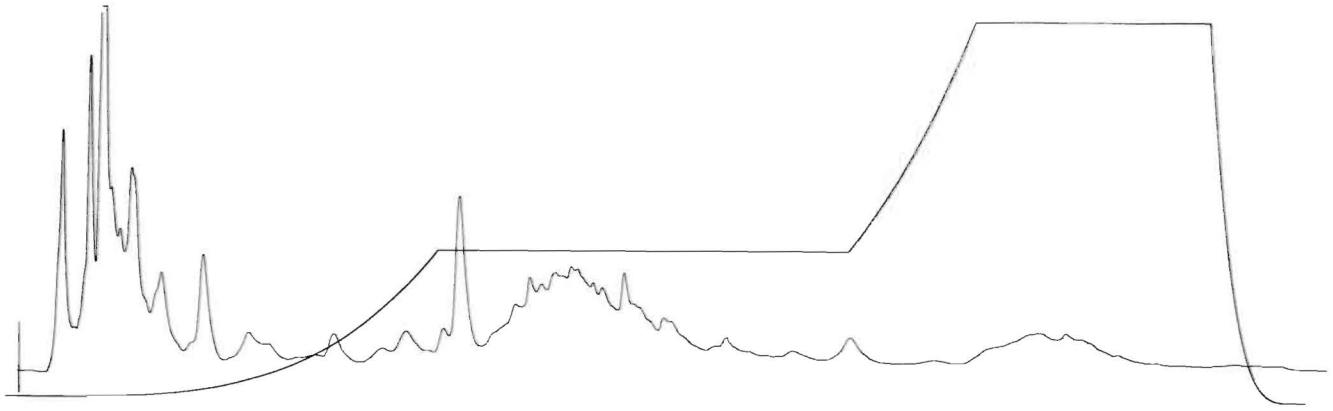

Figure 5. Liquid Chromatogram Partisil ODS, 254 nm. Detector Wavelength.

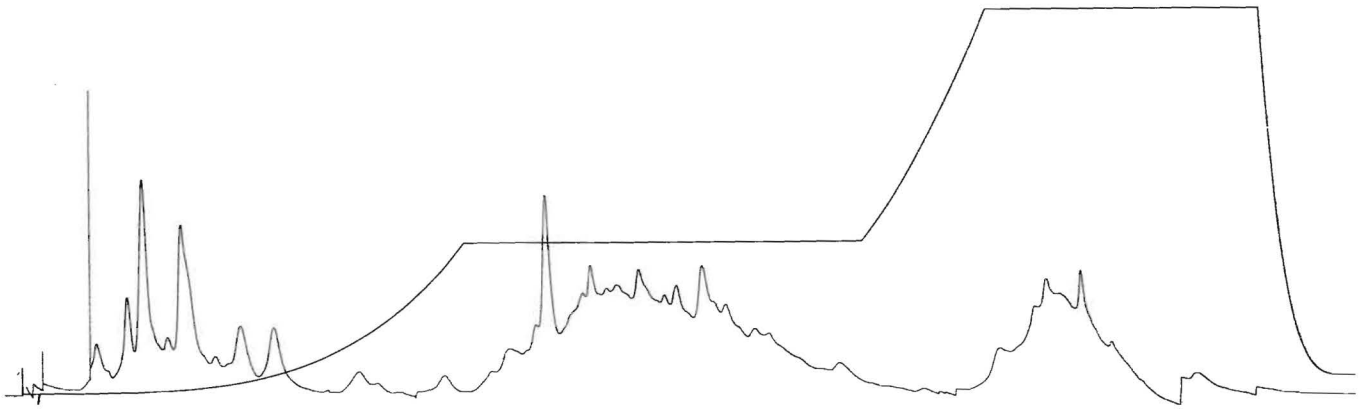

Figure 6. Liquid Chromatogram Partisil ODS, 280 nm. Detector Wavelength.

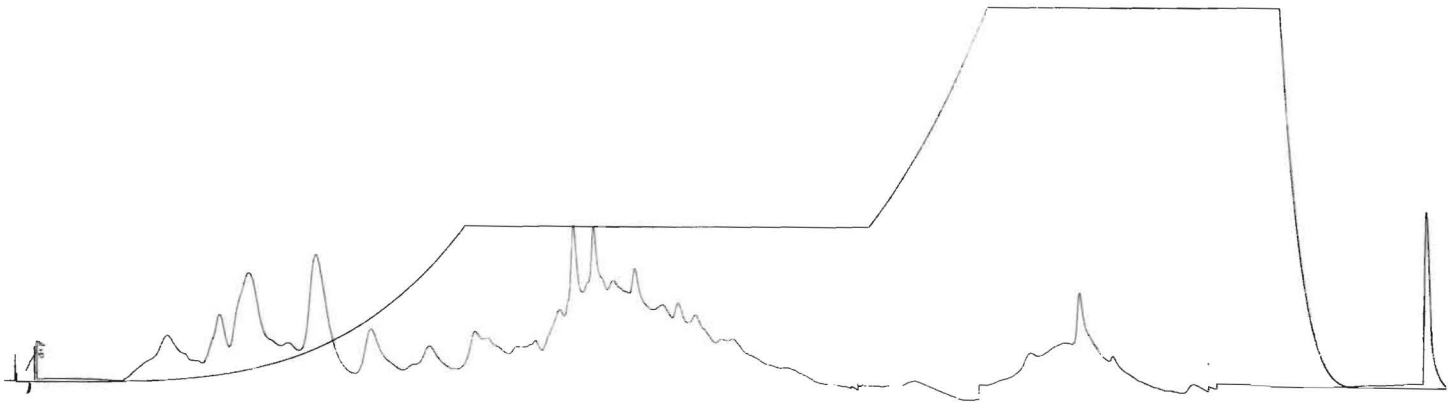

Figure 7. Liquid Chromatogram Partisil ODS, 300 nm. Detector Wavelength.

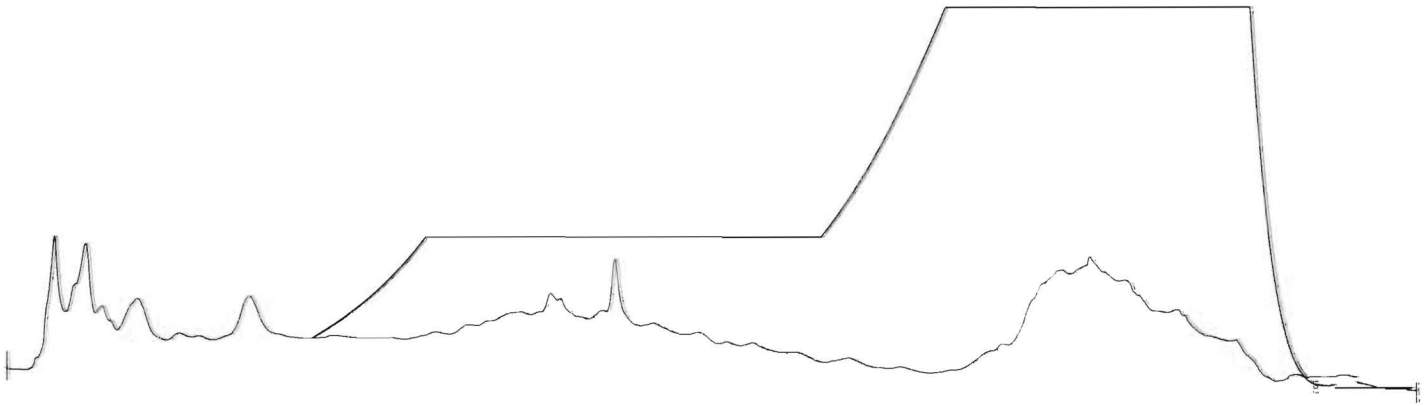

Figure 8. Liquid Chromatogram Partisil ODS, 360 nm. Detector Wavelength.

than condition 2. Condition 2 was selected to be a standard gradient with condition 1 being used for survey scans.

C. Flow Rate

1. Flow rates of 1 ml/min, 2 ml/min and 0.5 ml/min were tried, and 1 ml/min was chosen because it produced the best resolution consistent with a practical time limitation of 1 hour per L.C. run.

Ultraviolet Spectral Scans

In connection with the liquid chromatographic testing, ultraviolet spectral scans of some of the resolved components from the raw oil were made as follows. A Tracor 970 variable wavelength L.C. detector was used in the stopped-flow mode to scan individual spectra of resolved components from 400 nm. to nm. The output was plotted on a Houston HR-100 X-Y recorder. An example of this method is shown in Figures 9 and 10. The results of this study explains why there is so much peak response variability in the L.C. wavelength response study above. This technique will possibly be used as an identification aid for components along with infrared spectra.

Gas Chromatographic Procedures

Gas chromatography (G.C.) offers an excellent technique for analyzing complex mixtures of organic compounds. The apparent disadvantage in analyzing pyrolytic oils by G.C. is the heat sensitivity of some components in pyrolytic oils and the possible effect of the heat on these components during G.C. analysis. Recognizing this possible constraint, G.C. should be useful for analysis for fractions containing more volatile components and for water soluble components. In addition, it was considered appropriate to do some analysis of the raw pyrolytic oils because of the powerful analytical capability of G.C. The instruments used were a Perkin Elmer Model 900 with a flame ionization detector with dual column and temperature programmed capability, and a Perkin Elmer Model 990 with thermal conductivity detector, dual column, and

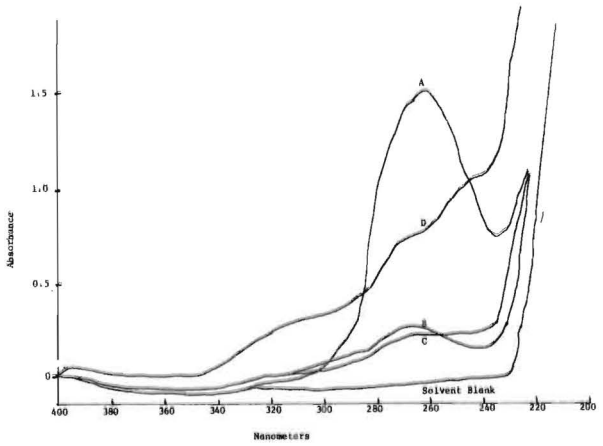

Figure 9. Ultraviolet Spectra of Peaks A thru D.

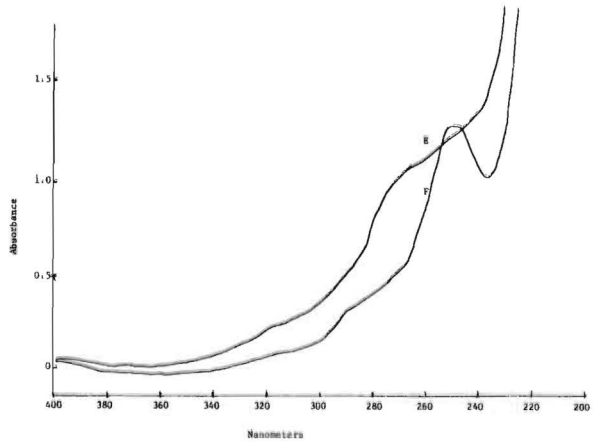

Figure 10. Ultraviolet Spectra of Peaks E thru F.

isothermal oven.

The objectives of this gas chromatographic work are to be able to resolve the low molecular weight components in the aqueous phases of various distilled fractions, to resolve the more volatile components of the oils and fractions of oil, and to analyze the higher molecular weight components of the relatively water-free pyrolysis oils and fractions obtained from the oils. To date, two columns were selected from several G.C. trial runs with the raw condenser oil and a distilled aqueous fraction. The list of columns and conditions that have been tried are given below.

Initial Conditions: P.E. 900 FID, carrier N_2 at 20 ml./min. Temperature program as shown. P.E. 990 T.C. detector, Helium carrier at 20 ml./min. isothermal oven. Samples screened were raw condenser oil and aqueous distillation fraction.

I. Porapak Q 9' x 1/8" with 1' x 1/8" Porapak Q precolumn to stop the heavy organics from entering the main column. Oven 120°C, injector 200°C, manifold 200°C, thermal conductivity detector 225 ma, Helium carrier at 20 ml./min. Results: The determination of water, lower alcohols, formaldehyde and acetone was accomplished.

II. 3% Poly-m-phenoxylene on 80/100 Chrom P. DMCS, 6' x 1/8". Injector 250°, manifold 250°, oven 130°C-200°C @ 8°/min. FID, N_2 at 20 ml./min. Results: moderate resolution of sample, 18 peaks, from raw oil.

III. 10% Dow Corning High Vacuum Grease on 80/100 AWFB-DMCS 10' x 48". Injector 340°, manifold 340°, oven 150°-350° @ 10°/min. FID, N_2 20 ml./min. Results: 48 peaks minimum resolution from raw oil.

IV. 1% Polyphenyether (6 ring) on 80/100 AWFB-DMCS 3' x 1/8" injector 250°, manifold 250° oven 130°-250° @ 10°/min. FID, N_2 20 ml./min. Results: moderate resolution of sample, 23 peaks from raw oil.

Viscosity Measurements

Satisfactory viscosity measurements of pyrolytic oil have often been difficult to obtain when data of the viscosity versus temperature has been needed. A study is underway utilizing a Brookfield recording viscometer and Thermosel sample container to obtain viscosity vs temperature curves of pyrolytic oils and fractions for evaluation. An example of this type of curve is shown in Figure 11. The data from the Thermosel system agreed well with points taken laboriously by hand using a hot plate which required much longer times for equilbrium temperatures to be reached.

Molecular Weight Determinations

The results from the processing of pyrolytic oils, particularly when subjected to heat, indicate that reactions occur which produce higher molecular weight components. It is also desirable to have information on the molecular weight distribution of the raw pyrolytic oils. In an attempt to obtain some information on the molecular weight of the oils and fractions of oil, the newly available size exclusion liquid chromatographic columns of silica gel with narrow pore size distribution were utilized. The column selected was a 25 cm. column of DuPont SE-60 controlled pore size deactivated silica. This column has a molecular weight range of linear operation of approximately 100 to 800 $\bar{M}w$. Polystyrene standards of 800, 2200 and 9000 were obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania. Benzene, molecular weight 78, was also used. In these L.C. runs, the solvent was tetrahydrofuran and the UV detector was set at 280 nm. The average molecular weights of raw pyrolytic oils and some oil fractions were obtained. In addition, the still bottoms from a commercial distillation of a pyrolytic oil was tested. The preliminary results from this initial work is given Table I.

TABLE I

Preliminary Average Moecular Weight Determinations

Sample Description	$\bar{M}w$	Comment
Raw Condenser Oil	160	-
Raw Draft Fan Oil	150	-
Still Bottoms from Atm. Distilled Oil	150	-

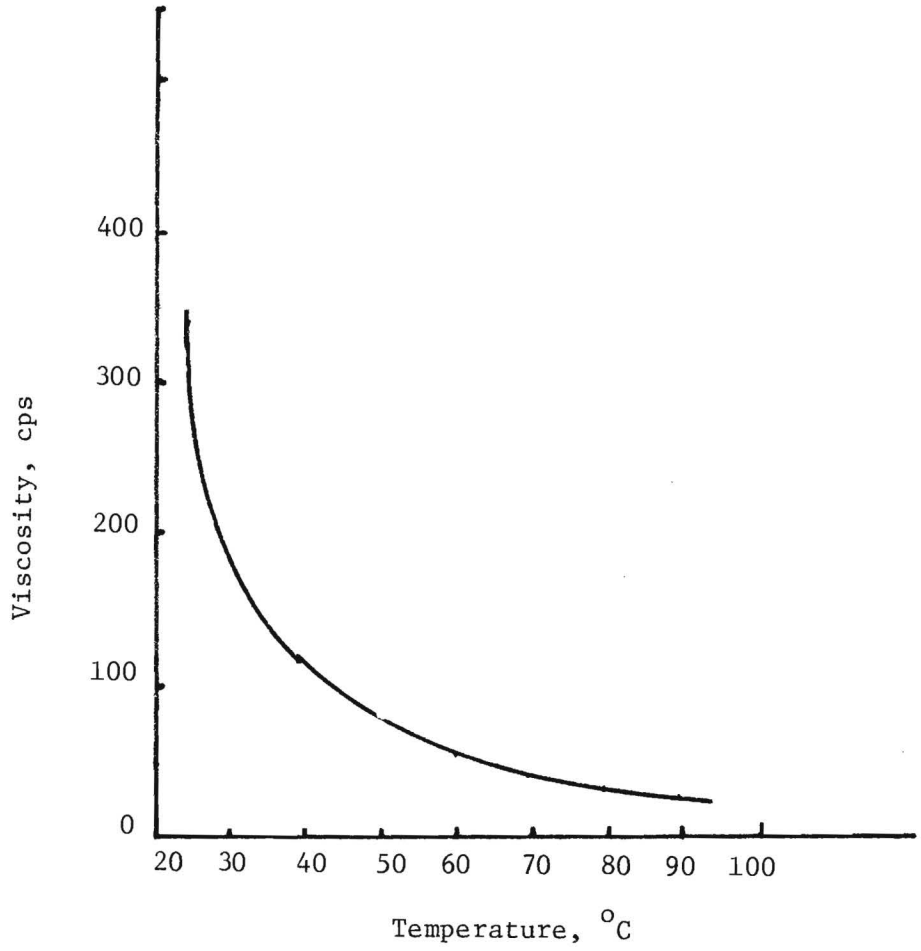

Figure 11. Viscosity Versus Temperature for Raw Condenser Pyrolysis Oil.

TABLE I (cont'd.)

Preliminary Average Moecular Weight Determinations

Sample Description	$\bar{M}w$	Comment
Vacuum Spinning Distillation Band Fract. 1-4	>100	-
Fract. 8	120 and 80	Two Main Components
Fract. 12	150	-
Still Bottoms Steam Distilled Oil	150	-
Still Bottoms from Commercially Distilled Oil*	112 - 9000	Broad $\bar{M}w$ Distribution

*Obtained from Tech-Air Corp.

DISCUSSION

The distillation experiments that have been carried out to date include atmospheric, simple vacuum, vacuum fractination and steam distillation. In addition, vacuum stripping of water and volatiles from the raw oil has been carried out. Considerable data has been obtained from these experiments and additional data will be obtained in order to assess and evaluate the results.

Analytical techniques are needed in this investigation of pyrolytic oils that can be used to follow the course of the processing method by analyzing the various fractions of oil to determine such things as degree of separation of components, number of components, and for comparison with known components for identification. Both gas and liquid chromatography are excellent techniques for obtaining high resolution of highly complex organic mixtures.

Liquid chromatography appears to be the method of choice as it can be carried out at ambient temperature. For this reason considerable effort was devoted to investigating this technique for use in our work with pyrolytic oils. The experimental details are given in the Experimental Work section along with the most suitable L.C. conditions developed to date for our study. Two important L.C. variables studied were the response versus detector wavelength and the solvent gradient rate variable. The effect of detector wavelength on response is probably the most significant variable studied in this attempt to develop the most suitable L.C. technique for our purposes. The samples shown in Figures 5 and 7 at 254 nm. and 300 nm. respectively illustrate the fact that the chromatograms appear to be two different samples but are in fact the same.

This selective response at different wavelengths suggests that individual generic types of compounds can be tuned in and their presence confirmed or qualitatively determined. The example that illustrates the selective response is shown in Figures 4 and 8 at 210 nm. and 360 nm. respectively. Here Figure 4 illustrates the detection of both aliphatic and aromatic components. Figure 8 illustrates only the detection of aromatic conjugate compounds that absorb at or above 300 nm. The solvent gradient rate variable had a considerable effect on the resolution of the mixtures as would be expected. It was determined that the solvent carrier system of 10% acetonitrile in water was the lowest concentration of organic solvent to water ratio that would yield a finely divided emulsion of the sample without forming an unmanagable precipitate on the head of the L.C. column. A logarithmic concave gradient performs the necessary retention of the initial strength of the acetonitrile carrier until the strongly polar initial peaks of most of the samples have eluted. Then a positive hold at 40% strong solvent for 21 minutes was empirically derived by trial and error to elute the lesser polar components. A completion of the L.C. chromatogram is obtained by raising the strong solvent strength from 40% to 100% acetonitrile in a logarithmic concave gradient with a 10 minute final hold at 100% which is sufficient to clear the column of all sample components. The effects of flow rate changes were not significant in that resolution was not improved by lowering the flow to 0.5 ml./min. Increasing the flow to 2.0 ml. produced a poorer chromatogram by crowding the initial peaks. The work with the L.C. analytical technique will be continued in an effort to improve its application and utility in the analysis of pyrolytic oils.

The L.C. technique, utilizing the conditions developed in our work, has been applied in our distillation work, and representative L.C. chromatograms are shown in Figures 12 through 22. Examination of these chromatograms will indicate the complexity of the raw oil (Figures 12 and 13) and of the fractions obtained from the oil. The chromatograms of the raw oils indicate at least 50 components. For information purposes, representative chromatograms are included for samples from the atmospheric distillation, Figures 14 and 15, simple vacuum distillation, Figure 16, vacuum fractionation with spinning band column, Figures 17, 18 and 19, vacuum stripping without heat, Figure 20, and steam distillation, Figures 21 and 22. It would not be appropriate to discuss in

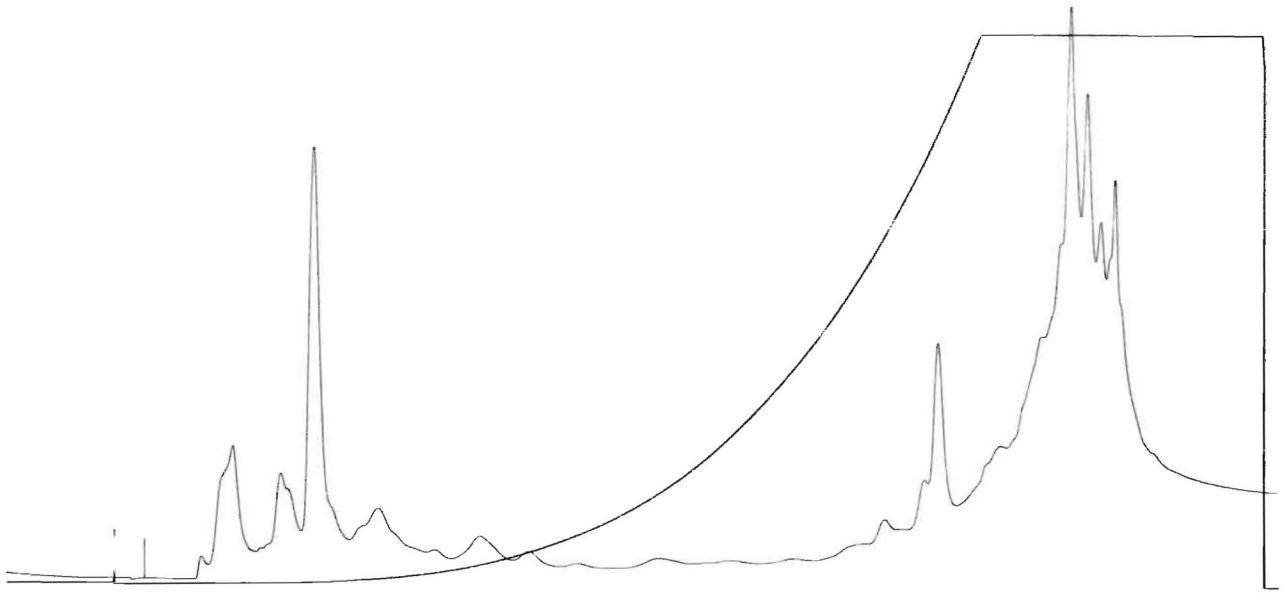

Figure 12. Survey Liquid Chromatogram Raw Condenser Oil.

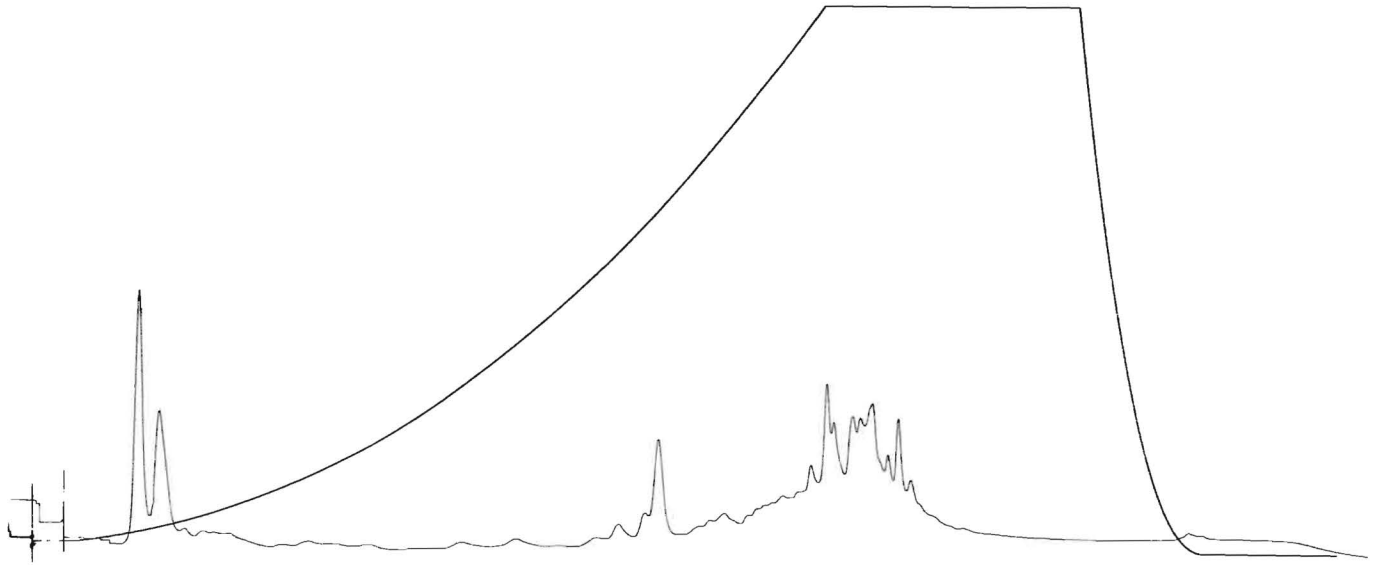

Figure 13. Survey Liquid Chromatogram Draft Fan Oil.

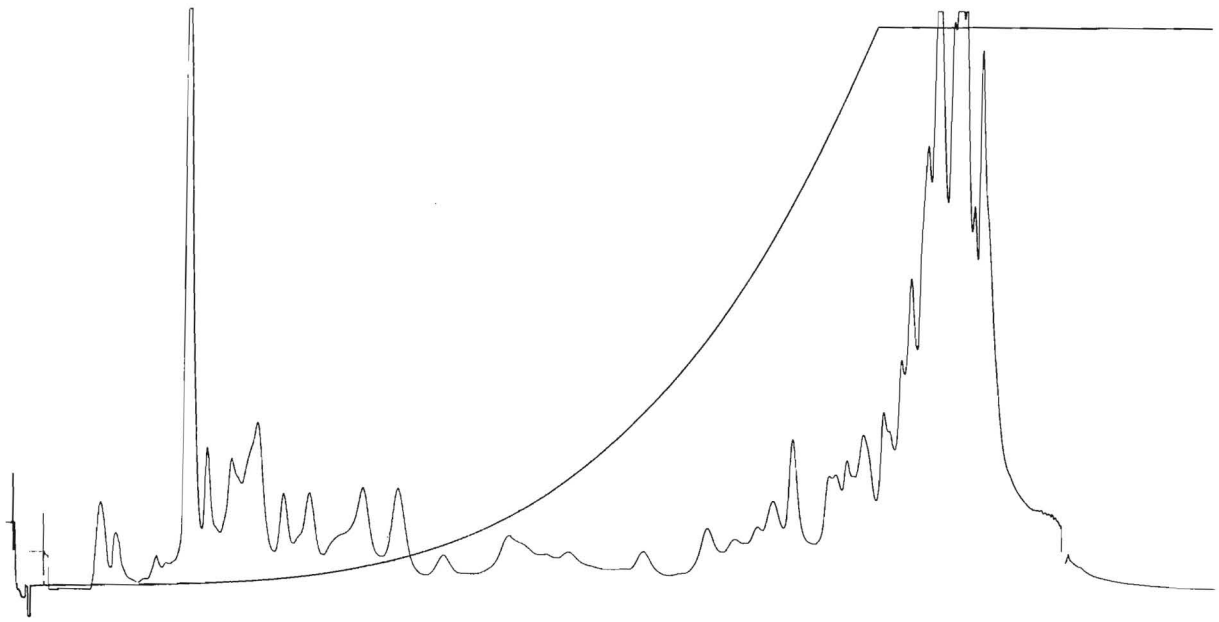

Figure 14. Survey Liquid Chromatogram Atmospheric Distillation Heavy Organic Layer.

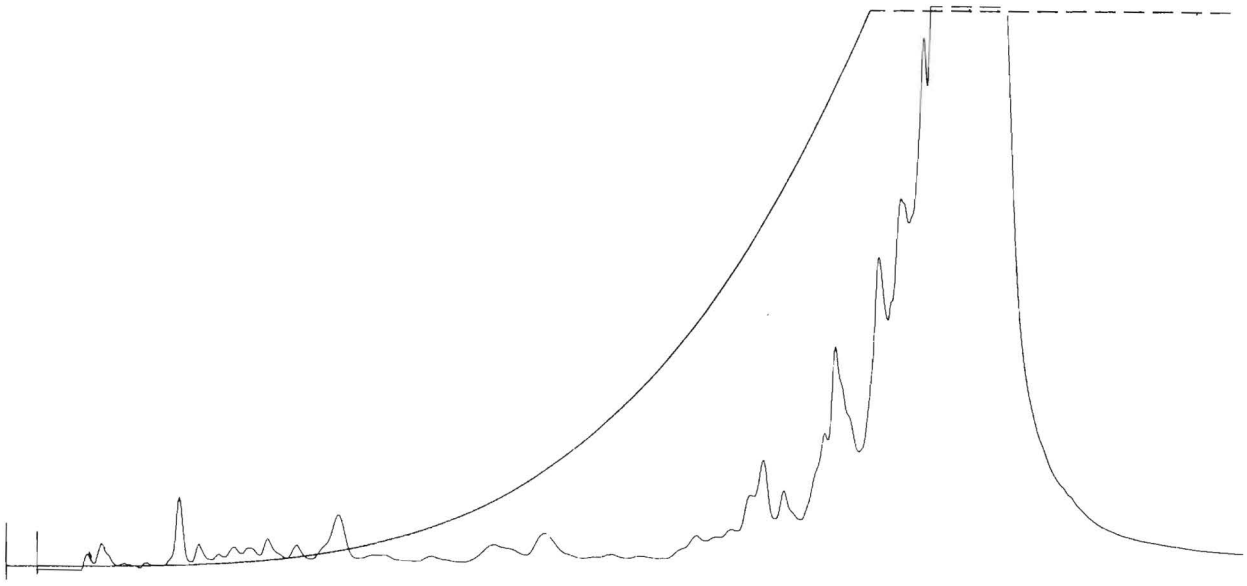

Figure 15. Survey Liquid Chromatogram Atmospheric Distillation Light Organic Layer.

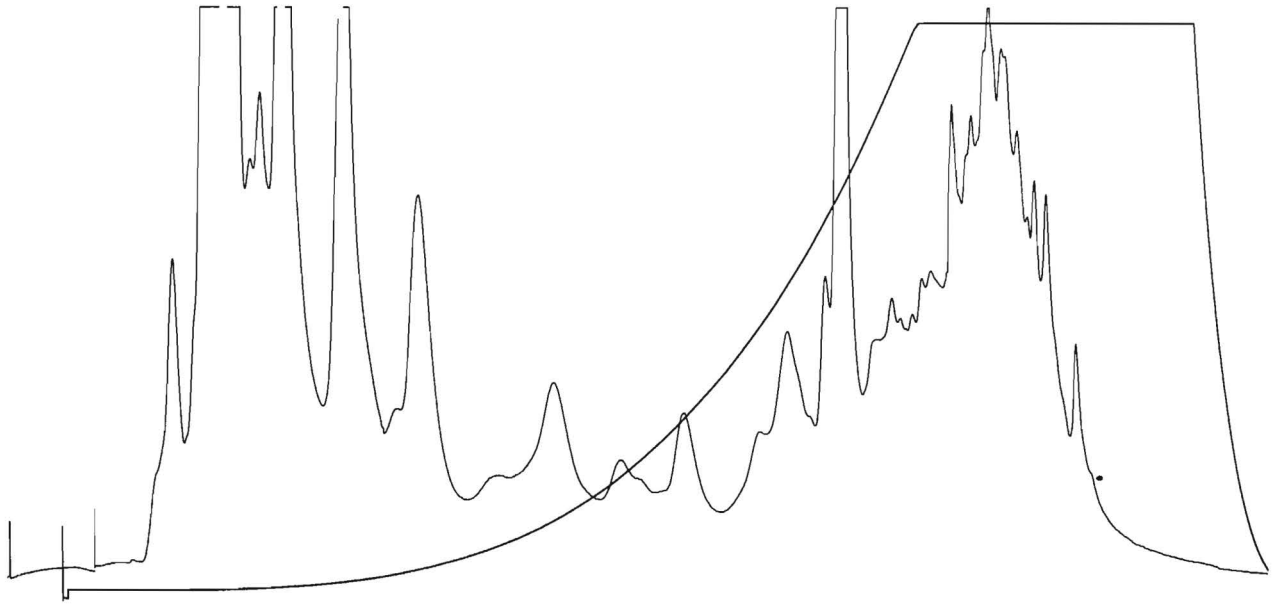

Figure 16. Survey Liquid Chromatogram Simple Vacuum Distillation Combined Fractions.

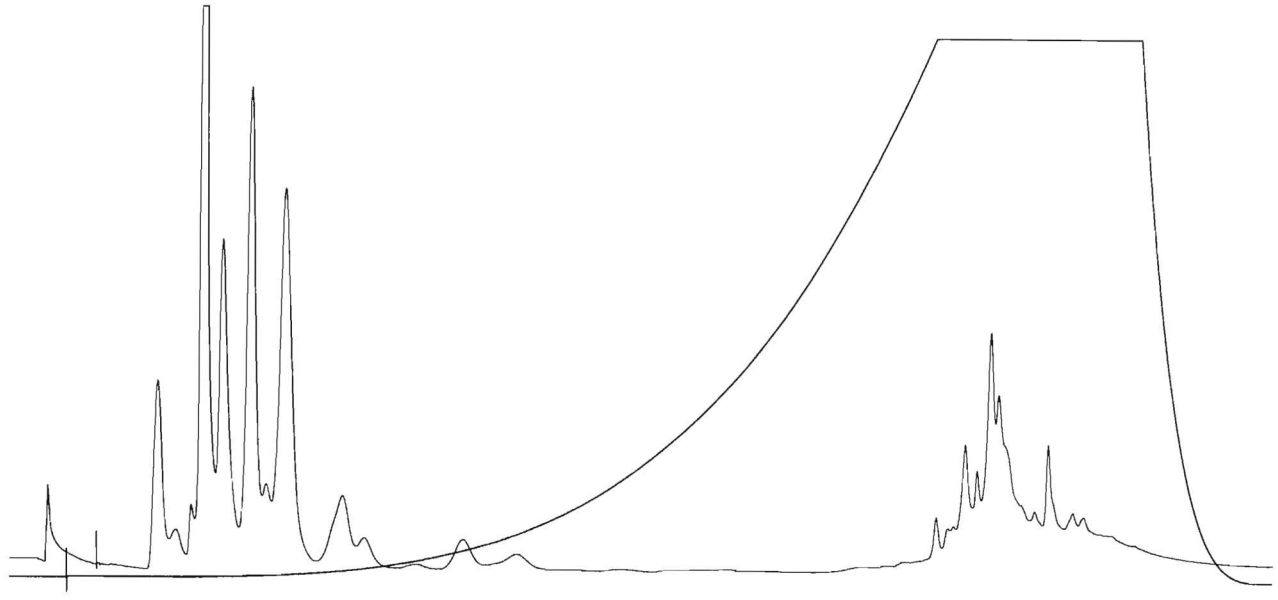

Figure 17. Survey Liquid Chromatogram Spinning Band 1-4 Fraction.

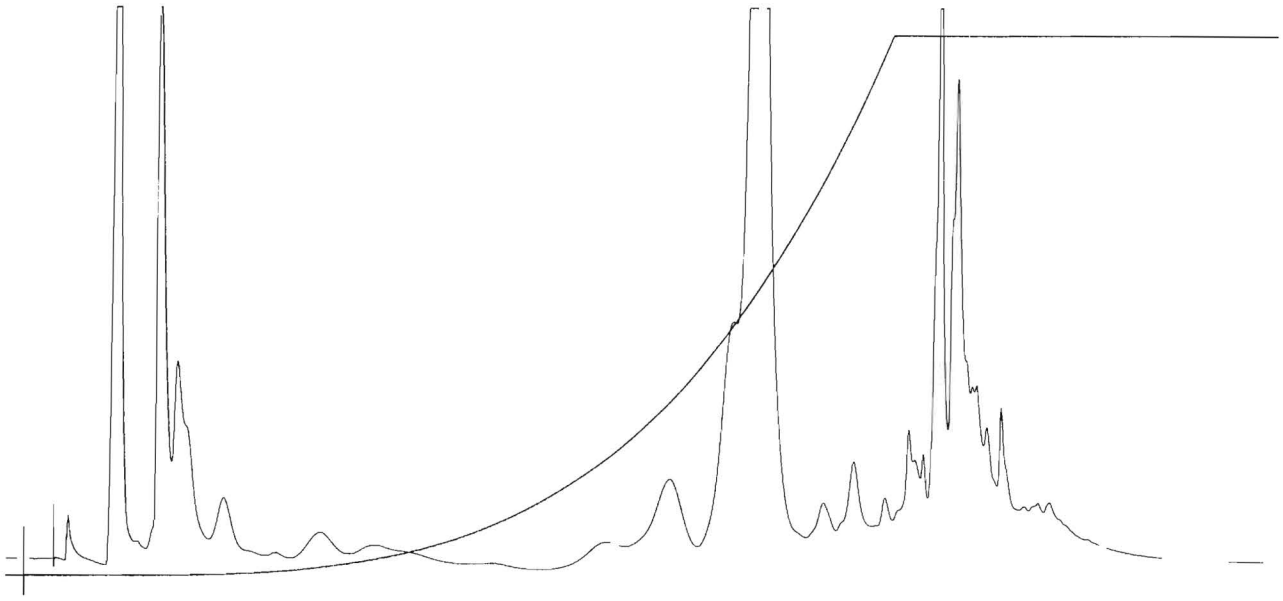

Figure 18. Survey Liquid Chromatogram Spinning Band 8 Fraction.

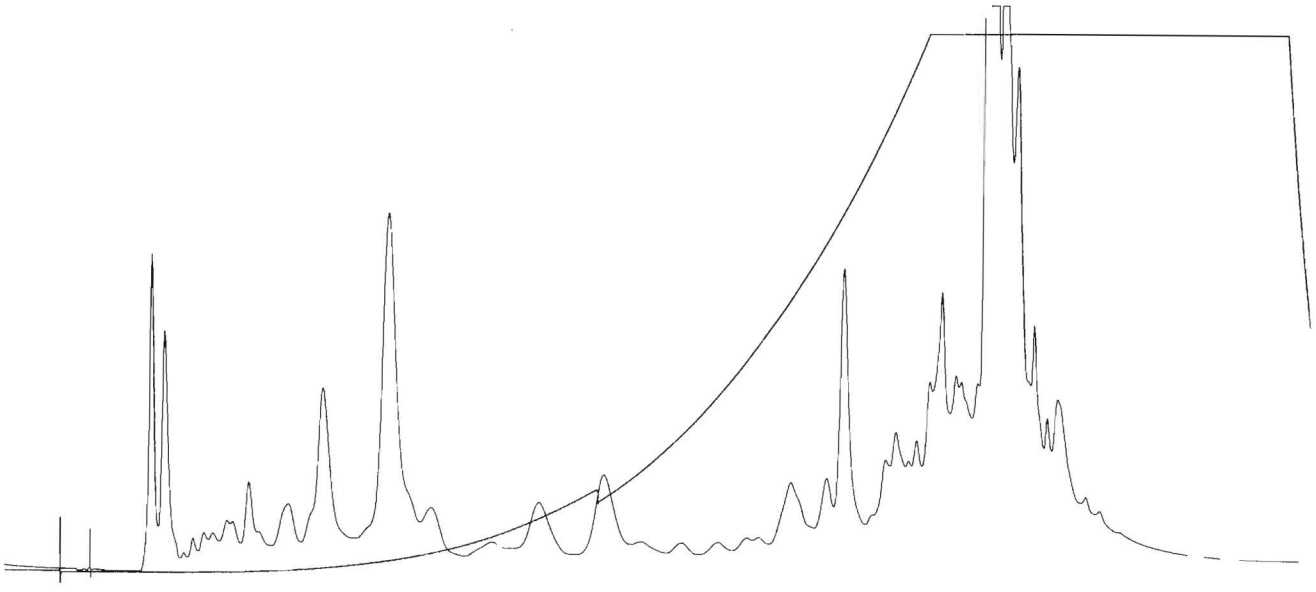

Figure 19. Survey Liquid Chromatogram Spinning Band 12 Fraction.

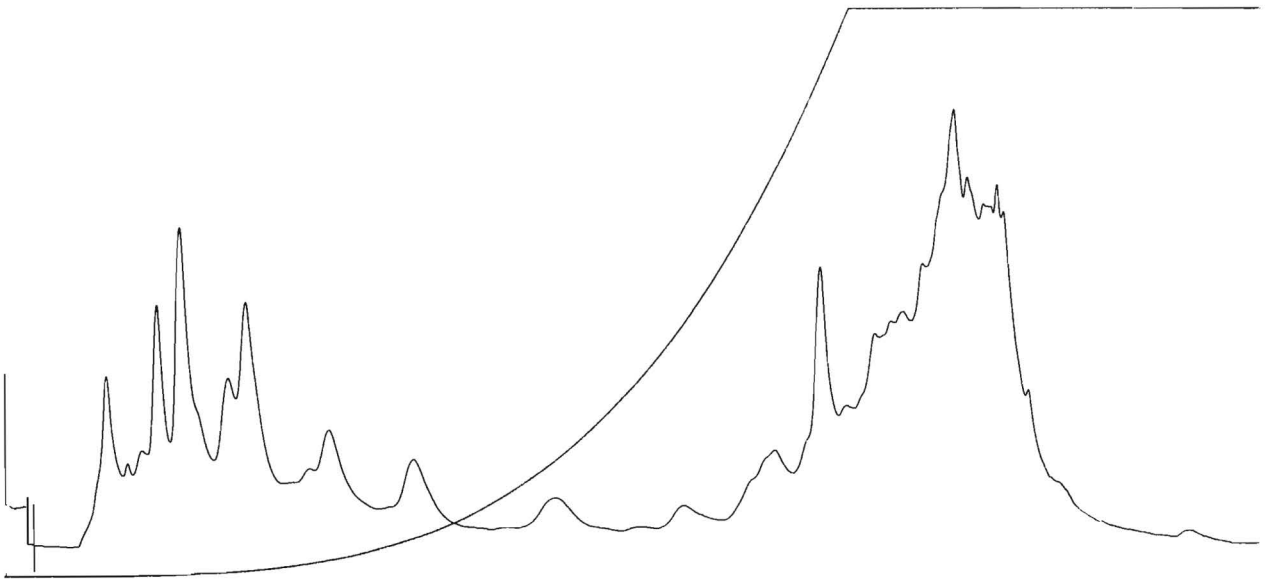

Figure 20. Survey Liquid Chromatogram Vacuum Stripped without Heat.

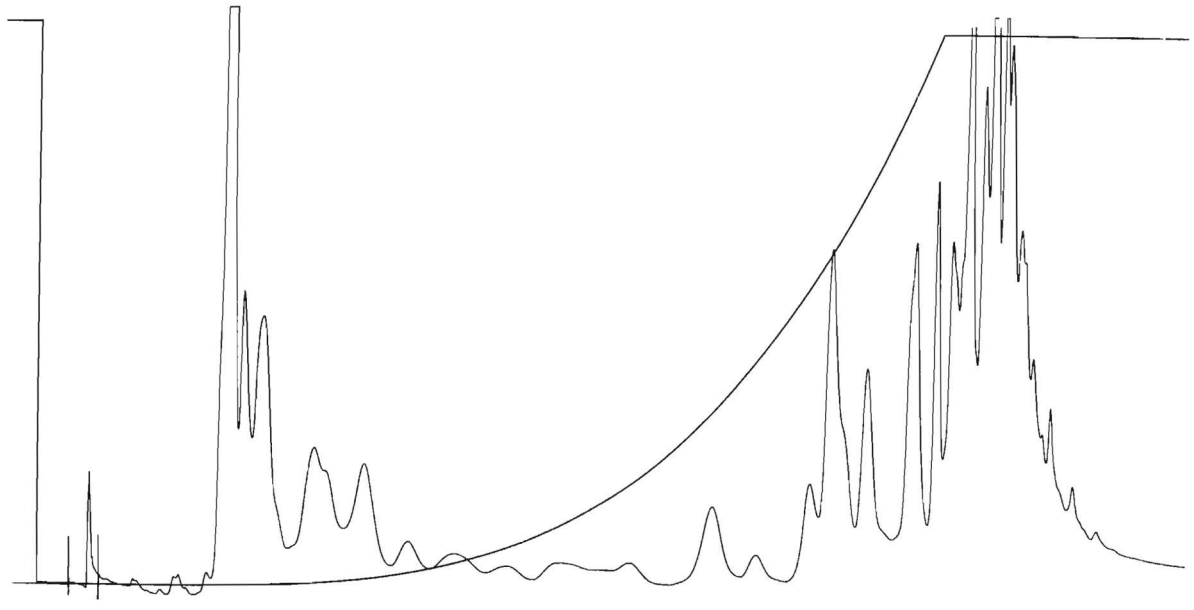

Figure 21. Survey Liquid Chromatogram Steam Distillation 100-105°C Organic Fraction.

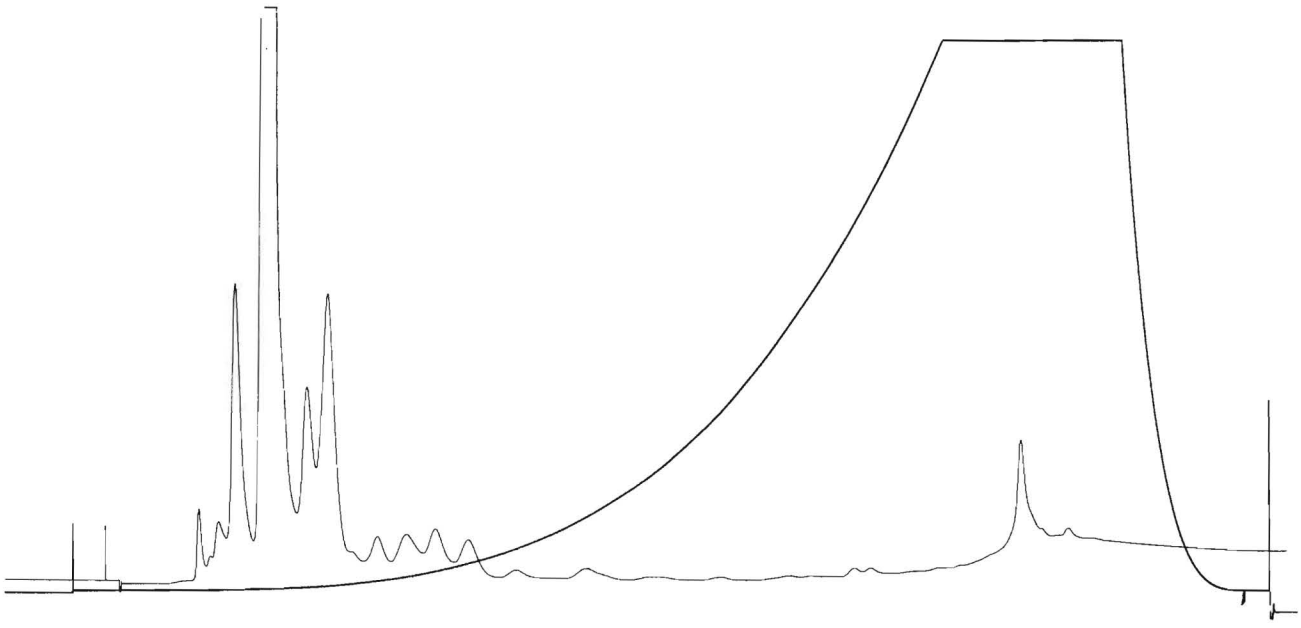

Figure 22. Survey Liquid Chromatogram Steam Distillation Aqueous Phase

in detail these data as the work is continuing.

Gas chromatography is also an important technique for resolving complex mixtures of organic compounds. Some work with G.C. has been done as an analytical tool for the raw pyrolytic oils and fractions obtained from them. Details are given in the experimental section. This work with G.C. is continuing in order to improve the conditions for analysis of pyrolytic oil samples. Two columns have been utilized to date. For aqueous samples obtained in the distillation of the pyrolytic oil, a Porapak Q column is used. For pyrolytic oil samples, a column with Dow Corning high vacuum silicone grease as the liquied phase was used. Representative gas chromatograms of the raw oil and from the distillation work are shown in Figures 23 through 34. A detailed discussion of the gas chromatograms would be premature at this time.

PUBLICATION

In the first quarterly report, it was reported that a technical paper, "Pyrolysis of Pine Sawdust," was presented at the Symposium on Thermal Properties, Pyrolytic Conversion and Combustion of Carbohydrates and Lignins, August 29--September 3, 1976, American Chemical Society, San Francisco. This symposium has been published in book form by Academic Press and is entitled, "Thermal Uses and Properties of Carbohydrates and Lignins," edited by Fred Shafizadeh, Kyosti V. Sarkanan and David A. Tillman. The reprint is presented in Appendix B.

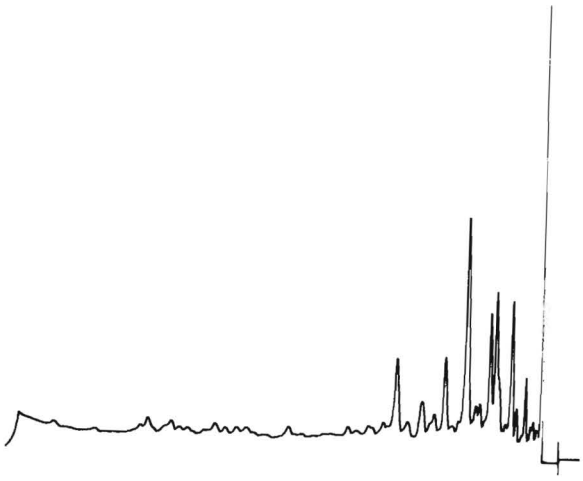

Figure 23. Raw Condenser Pyrolysis Oil Gas Chromatogram.

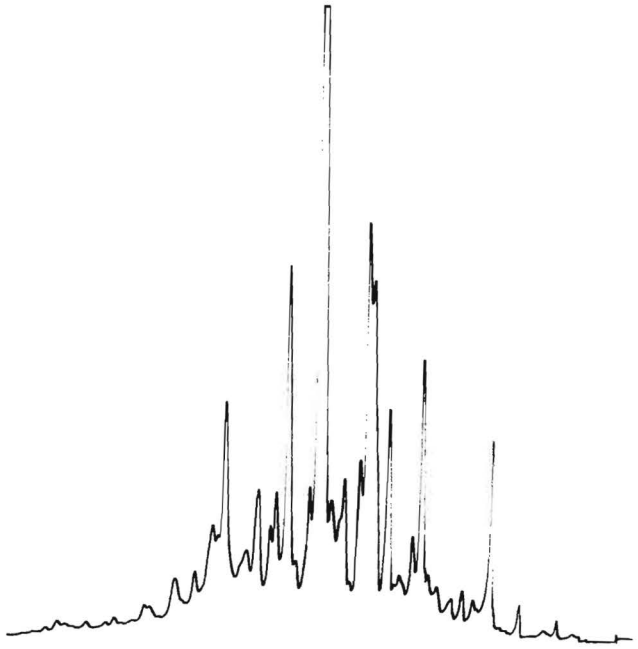

Figure 24. Steam Distillation First Organic Fraction Gas Chromatogram.

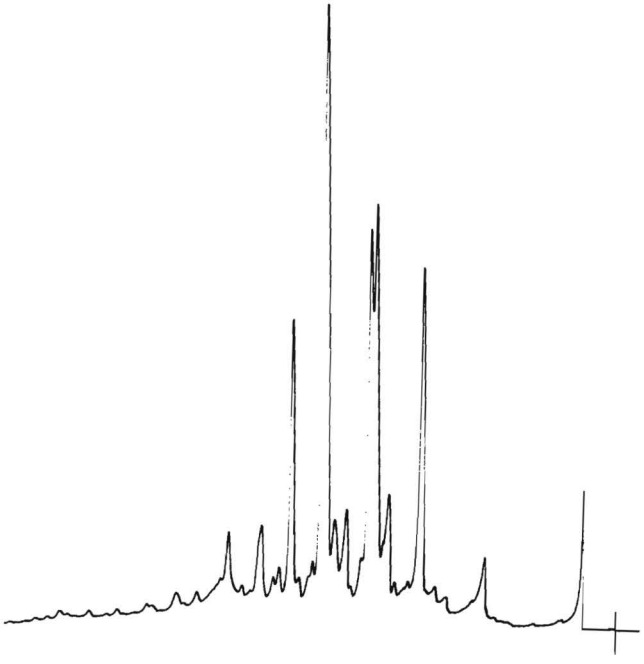

Figure 25. Steam Distillation Second Organic Fraction Gas Chromatogram.

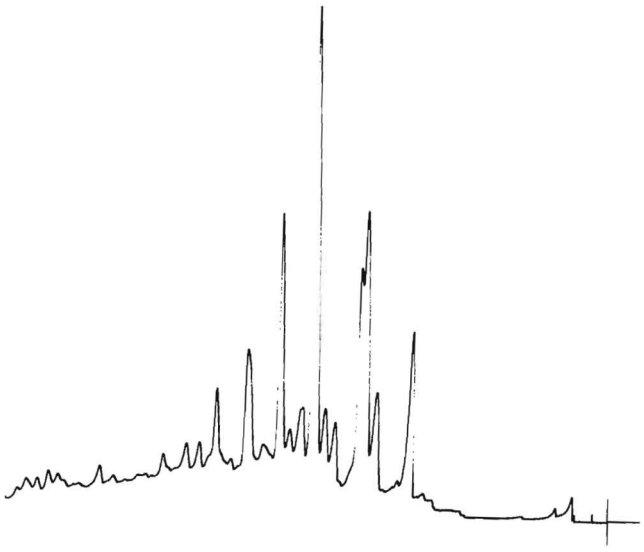

Figure 26. Steam Distillation Third Organic Fraction Gas Chromatogram.

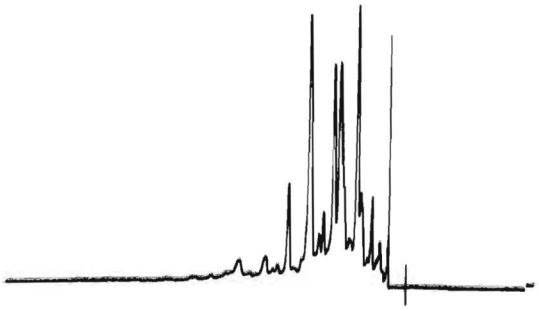

Figure 27. Simple Vacuum Distillation First Fraction Gas Chromatogram.

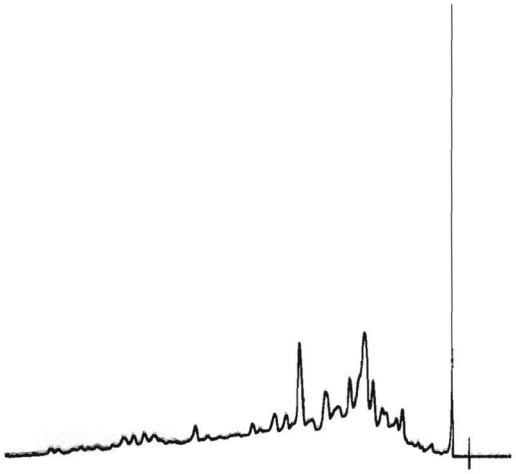

Figure 28. Simple Vacuum Distillation Third Fraction Gas Chromatogram.

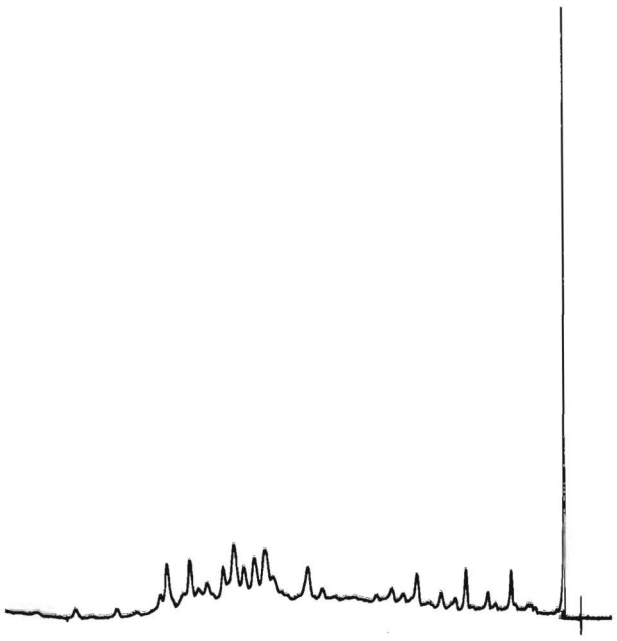

Figure 29. Simple Vacuum Distillation Fourth Fraction Gas Chromatogram.

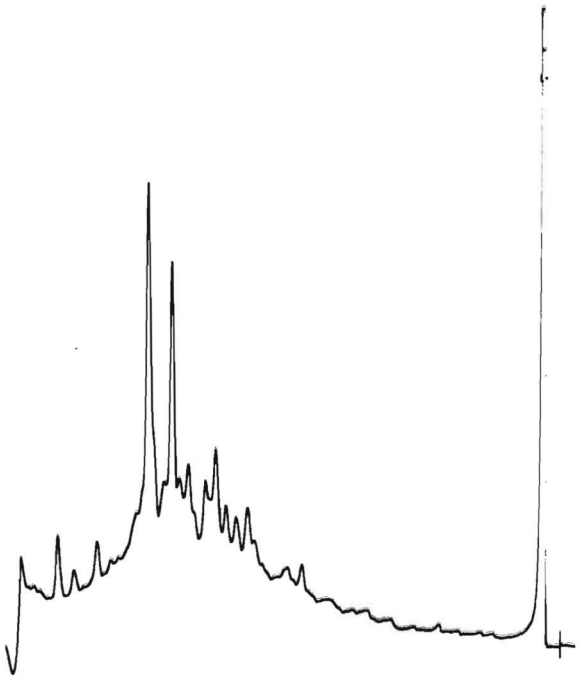

Figure 30. Simple Vacuum Distillation Bottom Residue Gas Chromatogram.

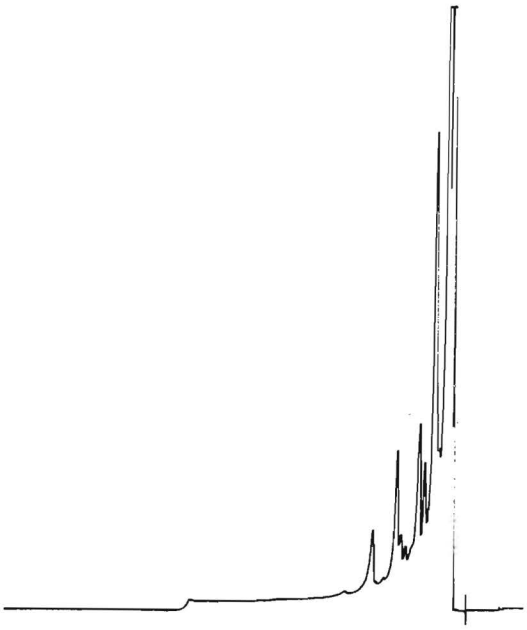

Figure 31. Simple Vacuum Distillation Aqueous Phase Gas Chromatogram.

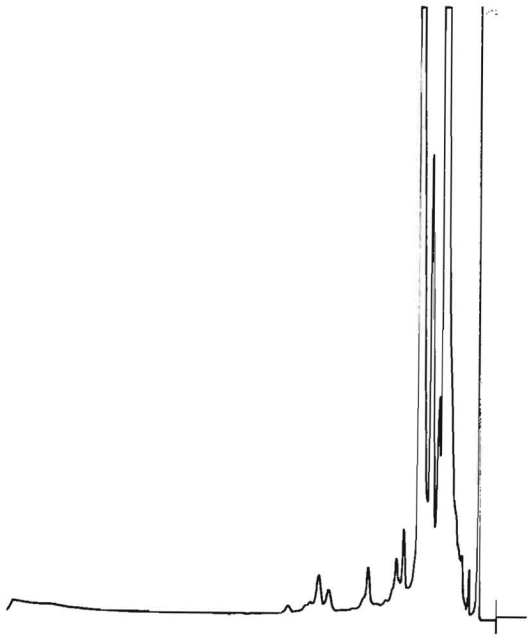

Figure 32. Spinning Band Vacuum Distillation 1-4 Fraction Gas Chromatogram.

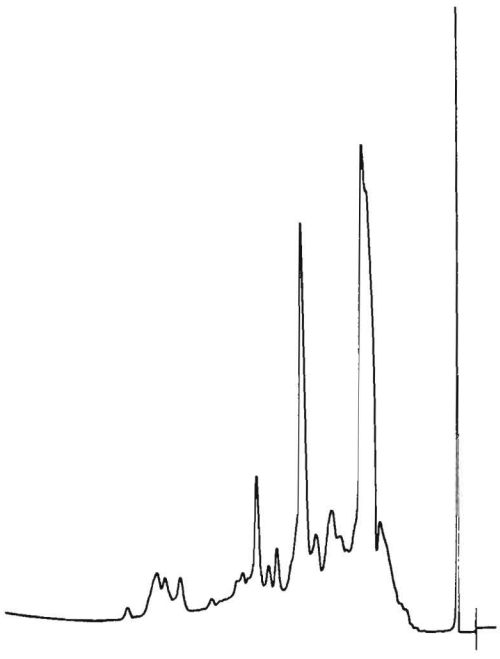

Figure 33. Spinning Band Vacuum Distillation 8 Fraction Gas Chromatogram.

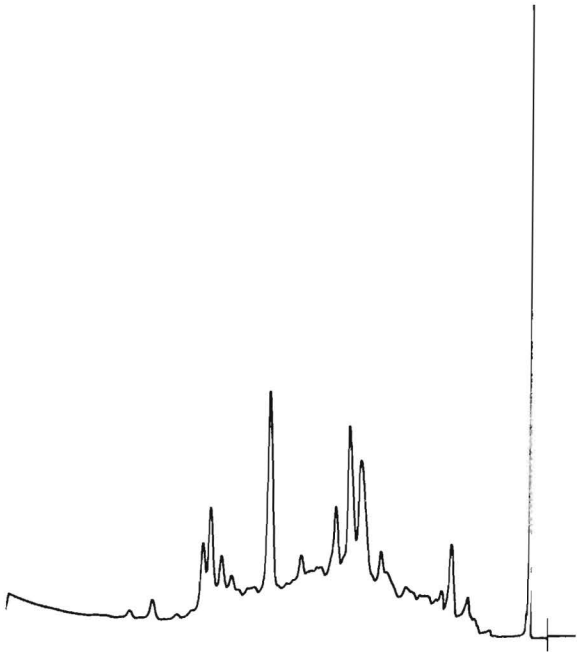

Figure 34. Spinning Band Vacuum Distillation 12 Fraction Gas Chromatogram.

EXPENDITURES

The expenditures from the initiation of the project through January 31, 1977, were as follows:

(a)	Direct wages and salaries	$ 15,156.50
	Retirement (9.1% of applicable wages and salaries)	1,377.43
	Travel	238.56
	Material and Supplies	1,503.01
	Capital	199.95
	Overhead (68% of direct wages and salaries)	10,306.42
	Total	$ 28,781.87
(b)	Total Budget	$ 65,000.00
	Expenditures through January 31, 1977	28,781.87
	Remaining Funds	$ 36,218.13

APPENDIX A

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APPENDIX B

Publication

"Pyrolysis of Pine Sawdust"
J. A. Knight
in
"Thermal Uses and Properties of
Carbohydrates and Lignins"

edited by

Fred Shafizadeh
Kyosti V. Sarkanan
David A. Tillman

Thermal Uses and Properties of Carbohydrates and Lignins

Edited by

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PYROLYSIS OF PINE SAWDUST*

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I. INTRODUCTION

The utilization of waste materials is of vital concern in the United States because these materials--agricultural, forestry, and municipal wastes--represent unused resources and in many cases present serious disposal problems. During the past several years, a great deal of attention has been given to pyrolysis as a means of converting these materials into useful products, particularly fuels. Workers at the Engineering Experiment Station (EES), Georgia Institute of Technology, have been utilizing the pyrolysis approach to convert agricultural and forestry wastes into char, pyrolytic oil and combustible gases [1-3]. Particular attention is being given to forestry wastes at the EES.

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These materials are abundant and in many cases are generated in large concentrated quantities at sites such as sawmills and paper mills and represent a relatively homogeneous material. In the United States, it has been estimated that 100 million dry tons of forestry wastes are generated annually [4]. Work with forestry wastes at the EES has been mainly with pine bark and sawdust because of their importance to the southeastern states. The EES has two continuous pyrolysis pilot plants that are used in research and development work in the pyrolysis of all types of lignocellulosic materials and municipal refuse. One of the pilot plants will process 1500 lb of dry feed per hour, and the other system will process 800 lb of dry feed per hour. The experiments reported in this paper on the pyrolysis of sawdust were conducted to provide data mainly on the yields of products, the heating values of the products, and compositions of noncondensible gases over the temperature range of 540°C to 870°C. These data are useful as guidelines in the operation of the two continuous pilot plant systems.

II. EXPERIMENTS

A. Feed Material

The feed material was pine sawdust and was dried to 6% moisture on a wet basis. The sawdust on a dry basis had 1.2% total ash. 0.3 acid insoluble ash, and a heating value of 8103 BTU/lb. The bulk density of the sawdust was 14.1 lb/ft^3, and 20% was +4 mesh, 68.0% was 4 x 16, 10.4% was 16 x 35, and the remainder (1.6%)was less than 35 mesh.

B. Pyrolysis

The pyrolysis experiments were conducted in a Lindberg Hevi-duty, 6 inch tube furnace (Fig. 1) fitted with a stainless steel tube (type 306). The furnace has three sections, which can be heated independently. Thermocouples were placed in the charge and the exit gas space. A charge of 2500 gm sawdust, 6% moisture on a wet basis, was held in place in the center of tube with spacers. The furnace was heated until the evolution gases had essentially ceased. The

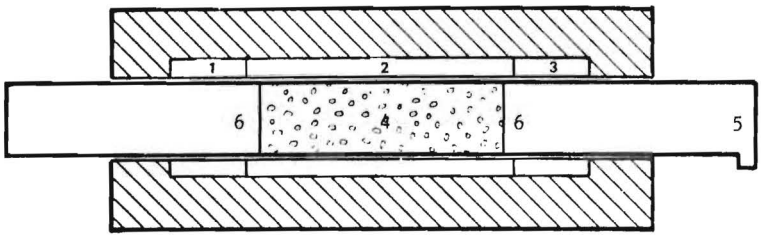

Fig. 1. Lindberg Hevi-Duty furnace; (1-3) furnace thermocouples, (4) thermocouple in center of charge, (5) thermocouple at gaseous exit.

temperatures of the furnace, in the center of the charge and at the gaseous exit, are given in Table I.

The temperature at the exit end of the tube was high enough so that condensation did not occur. The gas evolution rate for each experiment showed a rapid increase when the center of the charge reached the 150-175°C range and continued to evolve at a fairly rapid rate until the maximum temperature was reached. The off-gases were passed through a condensation train (Fig. 2) so as to condense the organic and aqueous material, and the gases were collected in large plastic gas-collection bags. Total volume of evolved gases were measured with a dry test meter.

At the end of a pyrolysis experiment, the ball valve (Fig. 2) was closed, and the char, after cooling to room temperature, was removed, weighed, and samples prepared for analysis.

TABLE I.

Maximum Temperatures During Pyrolysis

Location	Temperature (°C)			
Furnace	540	650	760	870
Middle of Charge	500	610	700-740	720-810
Gaseous Exit	230	280	320	360

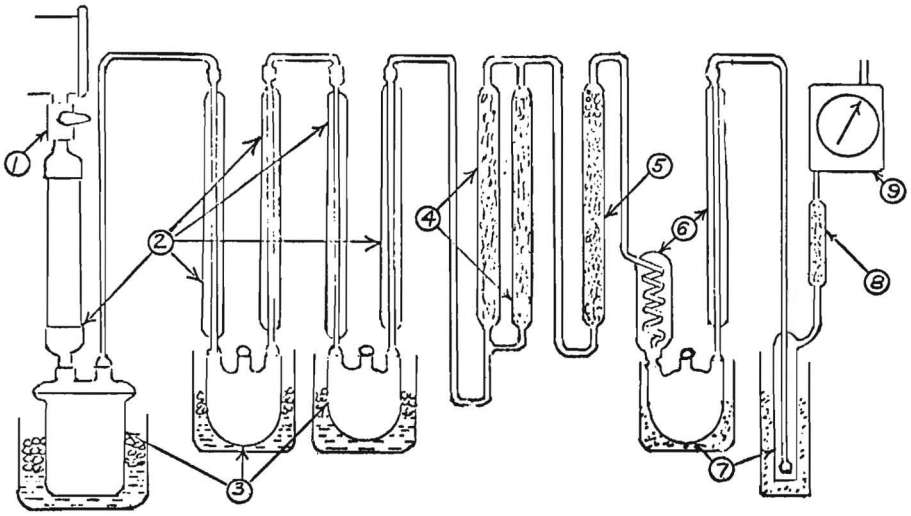

Fig. 2. Condensation train; (1) stainless steel ball valve, (2) water-cooled ball condensers, (3) ice-cooled traps, (4) glass wool demisters, (5) Drierite column, (6) cold condensers, (7) dry ice traps, (8) magnesium perchlorate dryer, and (9) dry test meter.

C. Condensation Train and Collection of Organic and Aqueous Phases

The off-gases from the pyrolysis tube pass through a stainless steel ball valve (1) [in Fig. 2] and then through a series of water-cooled condensers (2) and ice-cooled traps (3) (See Fig. 2). A jacketed stainless steel tube is used for the first condenser in place of a glass condenser. The use of a resin kettle as the first trap facilitates the recovery of viscous, oily condensates. The gas stream then passes through the two parallel glass-wool demisters (4) and a calcium sulfate (Drierite) column (5) into a series of cold condensers (6) and cold traps (7). The purpose of the demisters is to remove oil mist, and the calcium sulfate is used to remove the last traces of moisture from the stream. The cold condensers (6) are chilled with ethanol, which circulates through a heat-exchanger coil immersed in dry ice and

acetone, and the traps (7) are immersed in a bath of dry ice and acetone. From the cold traps, the gases pass through a magnesium perchlorate dryer (8) and a calibrated dry test meter (9) into a series of 96 liter gas-collection bags. The use of magnesium perchlorate has been found to present fouling of gas chromatographic columns during analysis of the noncondensible gases. The quantity of magnesium perchlorate is held to a minimum, and precautions are taken to prevent any explosion hazard. At the completion of an experiment, the weights of the condensates were stored in tightly closed containers. Heavy organic and aqueous condensates were stored at ambient temperature, and the condensates from the dry ice traps were stored in a freezer.

D. Noncondensed Gases

During the pyrolysis experiment, the gases were collected in 90 liter quantities successively in 96 liter gas-collection bags. After each bag is filled, it was kneaded to mix its contents, and approximately half of its contents were aspirated through gas-collection tubes (approximately 250 ml capacity). Two gas-collection tube samples were taken for analysis.

E. Analytical Procedures

1. Heating values

The heats of combustion of the feed material, chars, and organic liquids were determined in a Parr bomb calorimeter using the ASTMD-240-64 method.

2. Water in pyrolytic oils and aqueous phases

The percentage of water in the pyrolytic oil phases and aqueous phases was determined by a 2 hr distillation with toluene in a Dean-Stark apparatus. The percentage of water in the pyrolytic oils was generally less than 25%, and the percentage of water in the aqueous phase was generally greater than 75%. The ASTMD-95-70 (modified) was followed in these determinations.

3. Volatiles in char (Low temperature)

The weight loss in the char was determined by drying a weighed sample for 2 hr at 105°C followed by cooling 1 hr in a vacuum desiccator.

4. Volatiles in char (High temperature)

The volatiles in a char sample were determined by heating the sample from the 105°C determination at successive temperatures as follows: 2 min at 300°C, 3 min at 500°C, and 6 min at 900°C. The sample was cooled in a vacuum desiccator and then weighed to determine weight loss, which was calculated as percentage of volatiles.

5. Total ash

The char sample from the volatiles determination was ignited without the crucible cover to constant weight at 550-600°C, cooled to room temperature, and weighed.

6. Gas analysis

The gases were analyzed utilizing four gas chromatographic units, and the conditions are given in Table II.

III. RESULTS AND DISCUSSION

The yields of the four major pyrolytic products versus temperature are presented in Figure 3. The char yield decreases with increasing temperature and levels out at about 760°C. The yield of the combined oil condensates does not show any noticeable change with temperatures, except for the value at 760°C. This higher value may be due, in part, to an experimental error. The yield of the combined noncondensible gases increases with temperature, and the water yield decreases with temperature. The sums of the yields of all the products are within experimental error and show that essentially all of the products were recovered. These data are useful as guidelines in the operation of the two continuous pyrolytic pilot plants at the Engineering Experiment Station. One pilot plant has a capacity of approximately 1500 dry pounds per hour, and the other 800 dry pounds per hour.

TABLE II

Gas Chromatographic Analytical Conditions

Gas component	G.C. column	Temp. (°C)	Flow rate; carrier gas	Detector and Instrument
Hydrogen	Silica gel; 60 x 80 mesh, 6' x 1/8"	32	18 ml/min; argon	Thermal conductivity; Carle AGC
Oxygen, nitrogen, methane, carbon monoxide	Molecular sieve, 13 x; 60 x 80 mesh, 12' x 1/8"	40	20 ml/min; helium	Thermal conductivity; Perkin Elmer 990
Carbon dioxide	Activated carbon; 60 x 80 mesh, 10' x 1/8"	150	22 ml/min; helium	Thermal conductivity; Carle AGC
Hydrocarbons (C_2 to C_5)	Alumina F-1; 60/80 mesh	50-150 at 12°/min.	24 ml/min; nitrogen	FID; Perkin Elmer 800

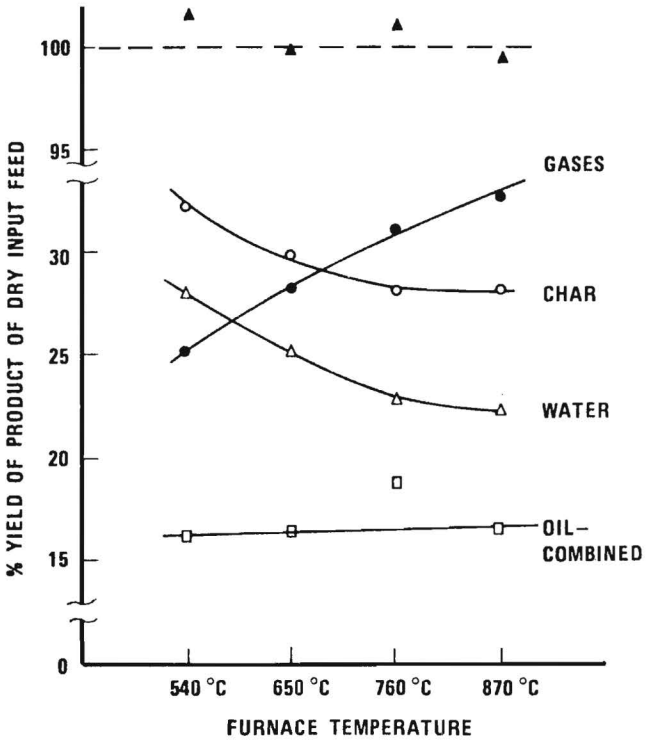

Fig. 3. Yields of the four major pyrolytic products versus temperature.

Analysis of the noncondensible gases showed that major gases are hydrogen, methane, carbon monoxide, and carbon dioxide. The C_2, C_3, and C_4 hydrocarbons are produced in relatively small amounts, and no experimental attempt was made to identify the individual components of these hydrocarbons. The variations of the yields of these gases are shown in Figure 4. The carbon monoxide and carbon dioxide both show significant decreases in yield with increasing pyrolysis temperature. The hydrogen yield shows a dramatic increase for the temperature range investigated. The methane yield increases to a maximum at approximately 680°C and then shows a gradual decrease at the higher temperatures. These data serve as guidelines for the expected yields of the major gaseous components in the operation of the EES pilot plants. Based on the gas composition, heating values of the gaseous

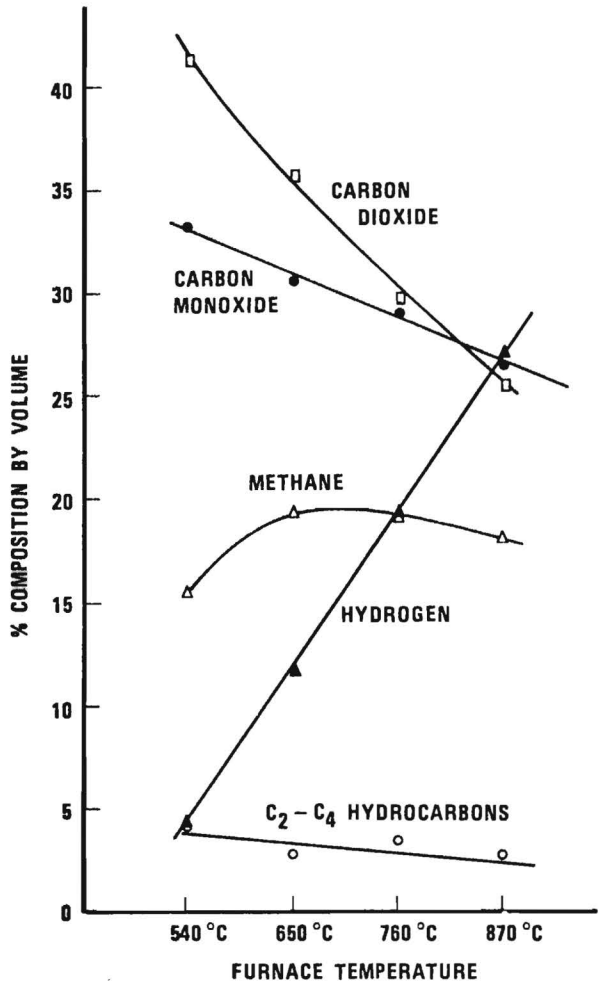

Fig. 4. Variations of yields of the major gases.

mixture produced at each temperature were calculated, and these are presented in Figure 5. The heating values of the pyrolytic gas increases with increasing temperature and shows a range of 350 to 410 BTU/ft^3. In actual practice in a continuous pyrolysis system, the heating value of the gas will be decreased by nitrogen from process air.

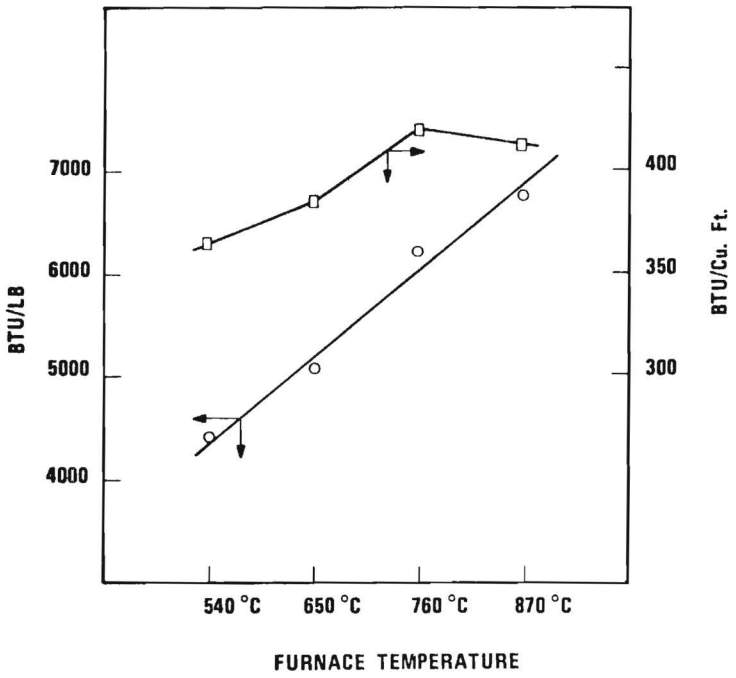

Fig. 5. Heating values of gaseous mixture produced at various temperatures.

The pyrolytic oil from the off-gas stream was collected into three different samples from the condensation train. The yields of each of these oils are presented in Figure 6, along with the combined yield. The reason for the higher yield values obtained for condensates 1 and 2 is not known. It is felt that they may be attributed in part to experimental error. Oil condensate 1 obtained from the first condenser represents the largest fraction and shows that the

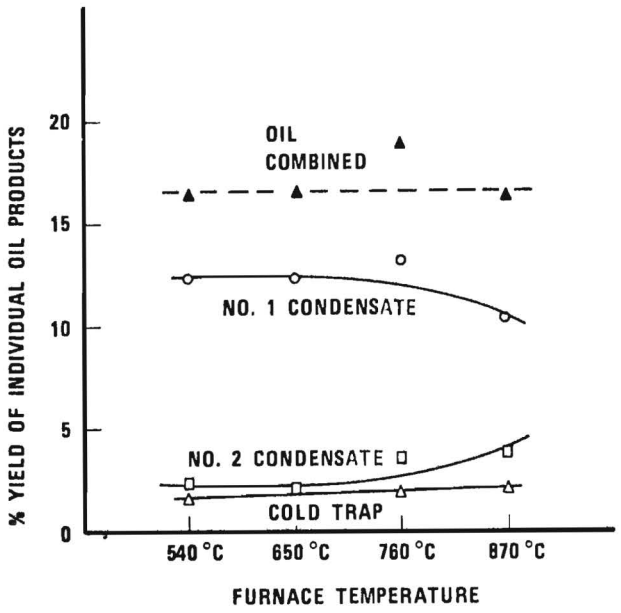

Fig. 6. Yields of pyrolytic oil from the off-gas stream.

oil yield decreases as the temperature decreases. Oil condensate 2 obtained from the next two condensers shows a slight increase with increasing temperature. The oil yield represented by the cold trap was condensed from the stream in a dry ice trap and was a relative volatile material. In actual practice in a continuous pilot plant operation, this oil would not be condensed from the off-gas stream and would add to the heating value of the gas. The heating values of the oils are given in Table III and are in the 12,000 to 14,000 BTU/lb range on a dry basis. In the operation of our continuous pilot plant pyrolysis units, the general practice is to operate the condenser so that the pyrolytic oil does not have more than 15% water. The remaining noncondensed gases, including water vapor, are burned in the afterburner.

The heating values of the pyrolytic products obtained at each temperature are given in Table III. In Figure 7, the heat available from each product versus temperature is

TABLE III
Heating Values of Pyrolytic Products

Product	Furnace temperature			
	540°C	650°C	700°C	870°C
Gas (BTU/lb)	4,411	5,029	6,205	6,771
Gas (BTU/ft^3)	348	362	395	409
Oil, first condensate (BTU/lb)	13,529	14,072	13,153	14,004
Oil, second condensate (BTU/lb)	12,158	13,555	12,637	12,716
Oil, dry ice condensate (BTU/lb)	13,362	13,643	13,290	13,432
Char (BTU/lb)	14,357	14,441	14,218	14,053

presented. The significant information to be gained from this graph is that the sum of the heats available from each product at each pyrolysis temperature is very close to the heat content of the dry input feed material. These data show that the total heat content of the input material is available for use in the three fuels--char, oil, and gas-- that are produced in the pyrolysis process. In Figure 8, the percentage recovery of each of the pyrolytic products of the input feed is presented. These data show that the heat values in the char and oil decrease with increasing temperature with more gas being produced. At 540°C, for example, the char and first oil condensate present 77.5% of the total heat value of the input feed, whereas at 870°C, they represent 66.7%. In order to obtain the maximum recovery of the heat content of the products, the gases must be utilized on site. A portion of the gases can be used for drying input feed, as the process operates best using feed material of less than 10% moisture.

Additional analytical data on the char samples is presented in Table IV. The significant information from this

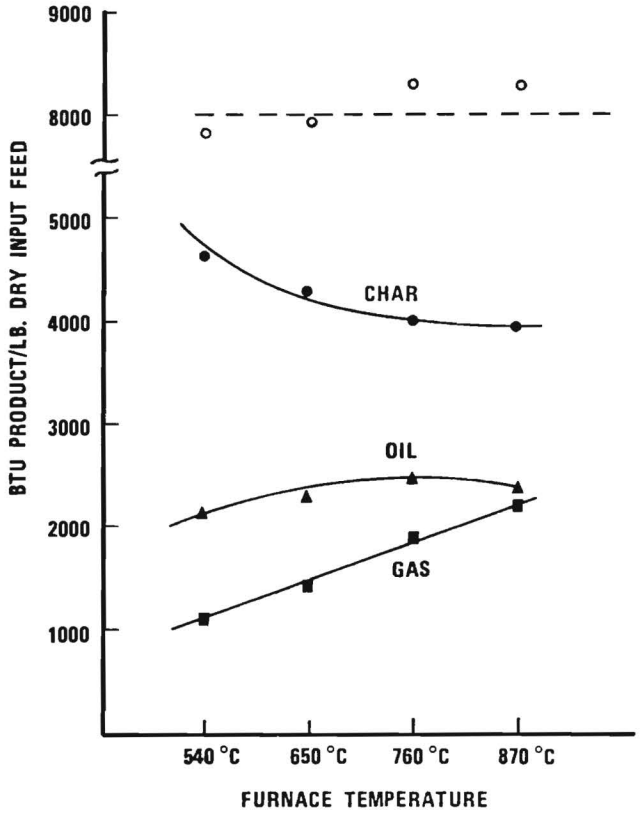

Fig. 7. Heat available from pyrolytic products.

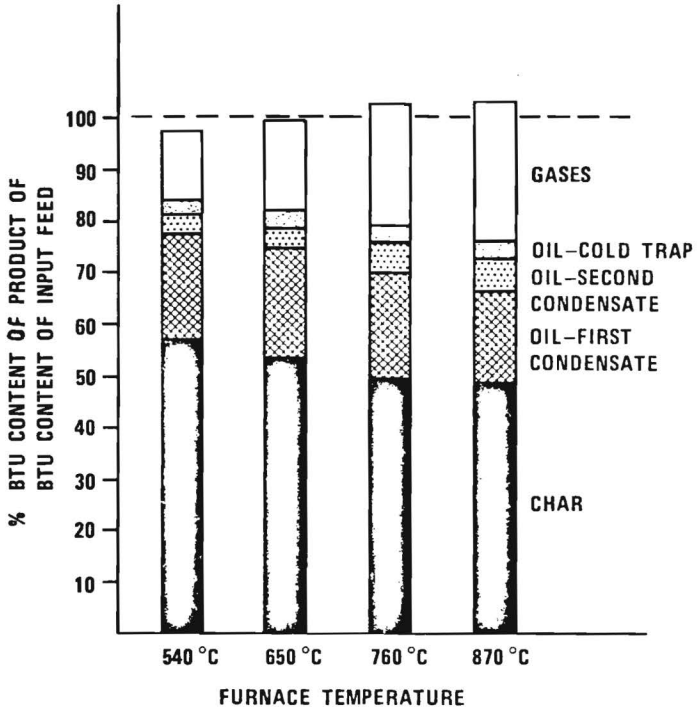

Fig. 8. Percentage of recovery of the pyrolytic products of the input feed.

table is the total volatiles in the char. The data show the temperatures that the char must be subject to in order to produce a char with a particular volatile content.

In summary, these bench scale pyrolysis experiments over the temperature range 540°C to 870°C provide data on the yields of the pyrolytic products, the composition of the gaseous phase, the heating values of the products, and the heat recovery in the different products.

TABLE IV

Char Analytical Data

	Furnace temperature			
	540°C	650°C	760°C	870°C
Weight loss at 105°C (2 hr) (%)[a]	1.1	0.5	0.6	1.0
Total ash (%)	2.3	4.6	3.6	3.9
Volatiles (%)	13.7	7.1	3.7	2.8

a. Weight loss probably due to vapors absorbed during cooling of char after pyrolysis.

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ENGINEERING EXPERIMENT STATION

Atlanta, Georgia

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by

J. A. Knight

Grant No. R 804 416 010

Performed for

Municipal Environmental Research Laboratory

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Cincinnati, Ohio 45268

ABSTRACT

The report summarizes the work on this project from June 21, 1976, to May 31, 1977. The broad objective of this study is to maximize the value of the oils obtained by pyrolysis of lignocellulosic materials, such as agricultural, forestry and municipal wastes, so that maximum resource recovery can be realized from these materials. For the initial phases of this study, wood oils from a 50 dry ton/day pyrolysis facility which processes pine bark and sawdust have been characterized and tested by a number of standard analytical procedures. Additional analytical procedures are needed to provide useful data for evaluation of oils that are produced from agricultural, forestry and municipal wastes by thermal degradation processes. The viscosity characteristics are important in the handling and processing of oils, and the viscosity-temperature curves of a number of these oils were measured. The results show that the viscosity is dependent upon the amount of water in the oil and its previous heat exposure history. These oils become more viscous when heated for extended periods. Liquid and gas chromatography have been used in analyzing the oils and fractions obtained from them by various processing techniques. Liquid chromatographic conditions have been developed for obtaining both survey and higher resolution liquid chromatograms of the oils and fractions from them. Preliminary molecular weight data indicate that the molecular weight range of the oils is 80 to 160. Distillation of the oils have been carried out at atmospheric pressure and low pressure (less than 1 mm mercury) using both simple vacuum and fractionation with a spinning band column. In the distillation of these oils, care must be exercised as the oils tend to start to decompose after about 60% to 70% of the oil has been distilled. The oils can be separated into fractions of closer boiling range. The data from liquid chromatography indicate that the lower boiling range fractions are more polar than the higher boiling fractions. Distillation of the wood oils is a processing method which can be used to obtain fractions that have potentially higher value uses than use of the oils as fuels. The wood oils are complex mixtures of organic compounds, are reactive and heat sensitive. They can be used as produced as a fuel oil if handled and burned in a proper manner, but have the potential for greater value use as chemical feedstock.

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FIGURES

FIGURES Cont'd.

FIGURES Cont'd.

TABLES

SECTION 1

INTRODUCTION

The utilization of the various quantities of agricultural, sivicultural and municipal wastes is of tremendous importance to the United States both from the standpoint of maximum resource recovery from these materials and as a means for disposal of waste materials in an environmentally acceptable manner. Pyrolysis has received considerable attention in the past few years as a conversion method for producing fuels and other products from these waste materials. Pyrolysis produces a char, organic substances, water, and noncondensible gases(1). The organic oils obtained from the off-gases from the pyrolysis of different lignocellulosic materials can be used as fuel. However, these oils have potential as a chemical feedstock and/or a source of organic chemicals and products. The broad objective of this study is to maximize the value of the oils obtained by pyrolysis so that maximum resource recovery can be realized from these materials.

The technical approach involves a thorough characterization of such oils and bench scale processing, such as distillation, of the oils to obtain preliminary data on the processing the oils and the different fractions and/or refined products that can be obtained from them.

For the purposes of this study, it was considered to be important that oil samples be obtained from a large scale pyrolysis facility. The Tech-Air Corporation* has a 50 dry ton/day facility in Cordele, Georgia, which processes a mixture of pine bark-sawdust on a continuous basis(2). Oil produced at such a facility would be more representative of commercial grade oil from pyrolysis processes than that produced in a laboratory batch system. For this study, samples of wood oils were obtained from the Tech-Air Cordele facility on two different occassions as described below in Section 2.

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* Licensee for the Georgia Tech--EES pyrolysis process.

This report covers the period June 21, 1976, through May 31, 1977, and describes the work on the different types of distillation experiments, the physical and chemical characterization of the wood oils and fractions obtained from them, and the utilization of liquid chromatography as a technique for "fingerprinting" the oil samples.

SECTION 2

EXPERIMENTAL

WOOD OIL SAMPLES - SOURCE

The wood oil samples were obtained from the Tech-Air field demonstration 50 dry ton/day facility while it was operating in a steady state mode processing a mixture of pine bark-sawdust. Wood oil samples were obtained on two occasions (July, 1976 and May, 1977) for use on this program. Each time, samples of oil were collected from the air cooled condenser and from the draft fan in the off-gas treatment system. A representative sample of the feed material, obtained in July, 1976, had the properties as listed in Table 1.

TABLE 1. PROPERTIES OF PINE BARK-SAWDUST FEED MATERIAL

Property	Results	Method
Pinebark / Pine sawdust	70 / 30	Microseparation by visual means
Bulk density	21.3 kg/cu m 13.3 lbs/cu ft	
Moisture	10.3%	ASTM D-1762-64
Ash (weight %)	1.3%	ASTM D-1762-64
Acid Insoluble Ash (weight %)	<0.1%	
Heating Value (dry basis)	5061 cal/g 9109 Btu/lb	ASTM D-240-74

CHARACTERIZATION OF WOOD OILS

Testing and Analytical Data

The wood oil samples were characterized by a wide variety of testing methods and analytical techniques. These results are given below in Tables 2 and 3 for samples obtained July, 1976, and May, 1977 respectively.

TABLE 2. PROPERTIES OF WOOD OILS FROM TECH-AIR 50 DRY/DAY FACILITY - OBTAINED JULY, 1976

Property	Condenser Oil	Draft Fan Oil	Method
Density	1.1415 g/ml 9.525 lbs/gal	1.1075 g/ml 9.242 lbs/gal	- -
Water content (weight %)	14.0%	10.4%	ASTM D-85-70
Heating Value (wet basis)	5,056 cal/g 9,100 Btu/lb	5,883 cal/g 10,590 Btu/lb	ASTM D-240-64
pH	2.9	3.3	5% Oil dispersed in water
Acid Number	75 mg KOH/g	31 mg KOH/g	ASTM D-664-58
Flash Point	111°C 233°F	121°C 240°F	ASTM D-93-73
Filterable Solids (weight %)	0.3%	0.4%	Acetone insoluble
Copper Strip Corrosion	1	1	Classification-ASTM D-130-7
Sulfur (weight %)	<0.01%	<0.01%	ASTM D-129-64
Pour Point	26.7°C 80°F	26.7°C 80°F	ASTM D-97-66
Ash (weight %)	0.08%	0.03%	-
Distillation			ASTM D-86
First Drop	98°C	101°C	Group 3
10% Point	103°C	105°C	
48% Endpoint	NA	265°C	
53% Endpoint	282°C	NA	
Solubility (weight %)			
Acetone	99.6%	99.6%	
Methylene chloride	93.5%	97.8%	
Toluene	Slightly	Slightly	
Hexane	Slightly	Slightly	
Elemental Analysis (weight %)			
Carbon	51.2	65.6	
Hydrogen	7.6	7.8	
Nitrogen	0.8	0.9	

TABLE 3. PROPERTIES OF WOOD OILS FROM TECH-AIR 50 DRY TON/DAY FACILITY - OBTAINED MAY, 1977

Property	Condenser Oil	Draft Fan Oil	Method
Density	1.352 g/ml 11.28 lbs	1.160 g/ml 9.68 lbs	-
Water content (weight %)	4.0%	31.4%	ASTM D-95-70
Heating Value (wet basis)	5,681 cal/g 10,225 Btu/lb	4,274 cal/g 7,694 Btu/lb	ASTM D-240-64
pH	3.0	2.8	5% Oil dispersed in water
Acid Number	57 mg KOH/g	75 mg KOH/g	ASTM D-664-58
Flash Point	——— *	——— *	ASTM D-93-73
Filterable Solids	0.07%	0.54%	Acetone insoluble
Copper Strip Corrosion	1	1	Classification-ASTM D-130-7
Solubility (weight %)			
Acetone	99.9%	99.9%	
Methylene chloride	61.2%	73.3%	
Toluene	Very slightly	Very slightly	
Hexane	Very slightly	Very slightly	

* Flash point determinations for these two samples were unsuccessful with the ASTM D-93-73 procedure. The condenser oil was extremely viscous at ambient temperature. No flash was noted with the condenser oil on heating to 175°C. With the draft fan oil, steam was given off at 110°C which extinguished the ignition flame of the Pensky-Martens closed cup tester.

Variation of Properties of Wood Oils with Time

Samples of the July, 1976, oils were stored at 0°C and ambient temperature for a period of approximately eight months and certain properties were redetermined. These data are presented in Table 4.

TABLE 4. VARIATION OF OIL PROPERTIES OVER EIGHT MONTHS PERIOD

Property	Condenser Oil*		
	Initial Value	Stored Eight Months	
		0°C	Ambient Temperature
Water Content (weight %)	14.0%	20.5%	21.1%
Heating Value (wet basis)	5,056 cal/g 9,100 Btu/lb	5,444 cal/g 9,800 Btu/lb	5,106 cal/g 9,190 Btu/lb
Acid Number	75 mg KOH/g	87 mg KOH/g	89 mg KOH/g
Viscosity†	275 cP	350 cP	175 cP
pH	2.6	3.4	2.9

Property	Draft Fan Oil*		
	Initial Value	Stored Eight Months	
		0°C	Ambient Temperature
Water Content (weight %)	10.4%	15.5%	12.7%
Heating Value (wet basis)	5,883 cal/g 10,590 Btu/lb	5,922 cal/g 10,660 Btu/lb	5,939 cal/g 10,690 Btu/lb
Acid Number	31 mg KOH/g	71 mg KOH/g	60 mg KOH/g
Viscosity†	233 cP	79 cP	475 cP
pH	3.3	3.1	3.0

* July, 1976, Samples.
† Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25° at 60r/min.

Comparison of Wood Oils and Fuel Oils

One significant use of these and similar oils is as a fuel. Therefore, it is of interest to compare some typical properties of the condenser and draft fan wood oils with number 2 and 6 fuel oils. These values are given in Table 5 below. It is of interest to note that because of the greater densities of the wood oils, the heating values of the wood oils when compared on a volume basis are larger percentages of the heating values of the fuels oils than when compared on a weight basis. The very low sulfur content of the wood oils is a significant property for the utilization of these wood oils as fuels. Proper blending of wood oils with high sulfur fuel oils can serve as a means of reduc-

ing the overall sulfur content of the combined fuel, and consequently, sulfur emissions.

TABLE 5. TYPICAL PROPERTIES OF WOOD OILS AND FUEL OILS

Property	Wood Oils*		Fuel Oils†	
	Condenser	Draft Fan	No. 2	No. 6
Water Content, %	14	10.4	Trace	2
Btu/lb	9,100	10,590	19,630	18,590
Btu/gal	86,700	97,850	139,400	148,900
Density, g/ml	1.142	1.108	0.851	0.960
lb/gal	9.53	9.25	7.10	8.01
Pour Point	80°F	80°F	0°max	65-85°F
Flash Point	233°F	240°F	100°F min	150°F
Viscosity, cP‡	225	233	20	2262
Elemental Analysis				
Carbon %	51.2	65.6	86.1	87.0
Hydrogen %	7.6	7.8	13.2	11.7
Nitrogen %	0.8	0.9	-	-
Sulfur %	<0.01	<0.01	0.6-0.8	0.9-2.3

* Values obtained on oils with moisture content as reported; July, 1976 samples.
† Values for fuel oils are considered typical. Sulfur will vary depending on origin of oil. Ref., North American Combustion Handbook, 1st ed., North American Mfg. Com., Cleveland, Ohio, 1952.
‡ Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25°C at 60r/min.

Viscosity

The viscosity of liquids and its change with temperature is a significant property, particularly with liquids that will be handled by pumping. The viscosity values for the wood oils in this study were determined with a Brookfield viscosimeter, Model LV, with Thermosel system. The viscosity versus temperature was determined for both the condenser and draft fan oils (July, 1976 samples) initially and on samples which had been stored at 0°C and ambient temperature for approximately eight months. These viscosity curves are given in Figures 1 and 2. The viscosity versus temperatures curves of samples of both oils which

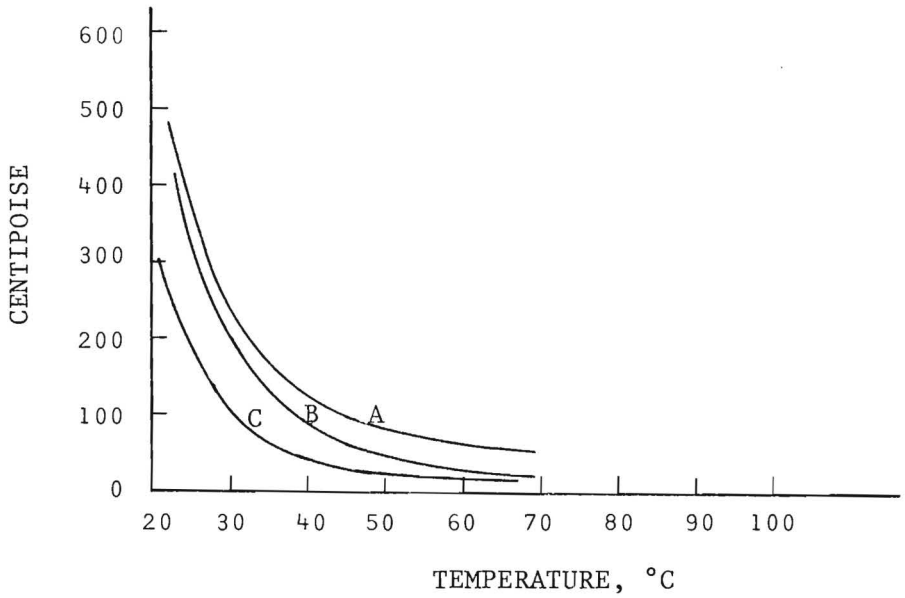

Figure 1. Viscosity of Condenser Oil

A - Initial viscosity curve

B - Sample stored at 0° C for eight months

C - Sample stored at ambient temperature for eight months

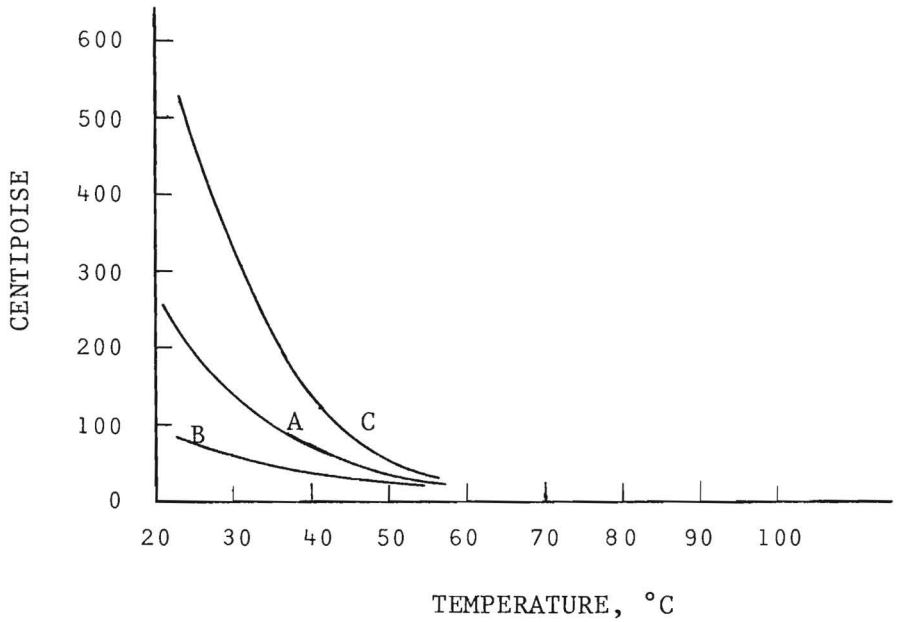

Figure 2. Viscosity of draft fan oil

A - Initial viscosity curve

B - Sample stored at 0° C for eight months

C - Sample stored at ambient temperature for eight months

had been vacuum stripped for removal of water are given in Figures 3 and 4. In order to determine the effect of prolonged heat upon the viscosity of condenser oil, samples of sealed oil were heated at 110°C for different time periods, and the viscosity was then determined for each sample. These data are presented in Figure 5. For comparison, the viscosities of the condenser oil and numbers 2 and 6 fuel oils are presented in Figure 6. The viscosity curves for the condenser and draft fan oils obtained in May, 1977, are given in Figure 7.

Liquid Chromatography (LC)

The wood oils are heat sensitive, reactive and contain a relatively large number of organic compounds. An analytical technique was needed which could be used in analyzing the fractions of oil obtained by the different processing methods that would not change the chemical character of the fractions. Liquid chromatography (LC) appears to be the method of choice because LC is carried out at ambient temperature, is capable of high resolution of complex mixtures, and component detection is nondestructive. In addition, the wood oils are soluble in organic-aqueous solvent systems which are very useful in LC. The main initial objective of utilizing LC in the work with the wood oils is to provide a method to obtain "fingerprints" of the raw oil and fractions produced from it for comparison and correlation.

Testing of LC Variables--

The variables that were studied to find satisfactory LC conditions were LC columns, uv wave length, solvent gradient and solvent flow rate. The condenser oil (July, 1976) was used for testing all of these variables.

LC Columns--In order to select the most suitable LC column, several columns were tested with the raw condenser wood oil (July, 1976) using one ml/min flow rate and uv detector at 254 nm. The chromatographic columns and conditions tested and the results are given below in the order in which the testing was carried out.

A. Vydac adsorption silica gel 30μ column. Solvent, 0-100% 2-propanol in isooctane, 20 min gradient 20 concave.*
   Results: No resolution obtained; only one large peak.

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* Term used as a dial setting for logarithmic slope control on Micrometritics LC models only.

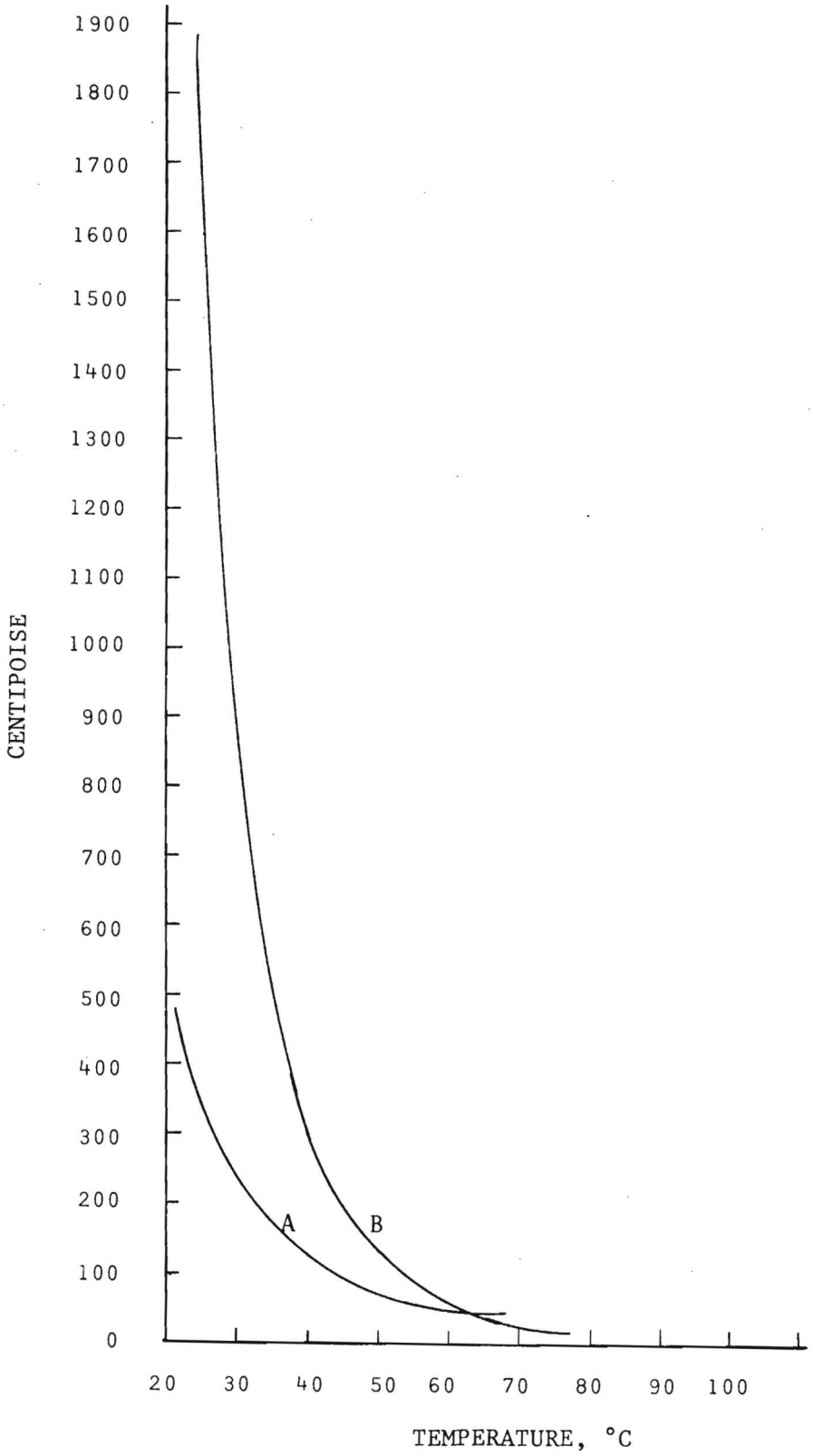

Figure 3. Vacuum Stripped Condenser Oil

A - Initial viscosity curve

B - Vacuum stripped viscosity curve

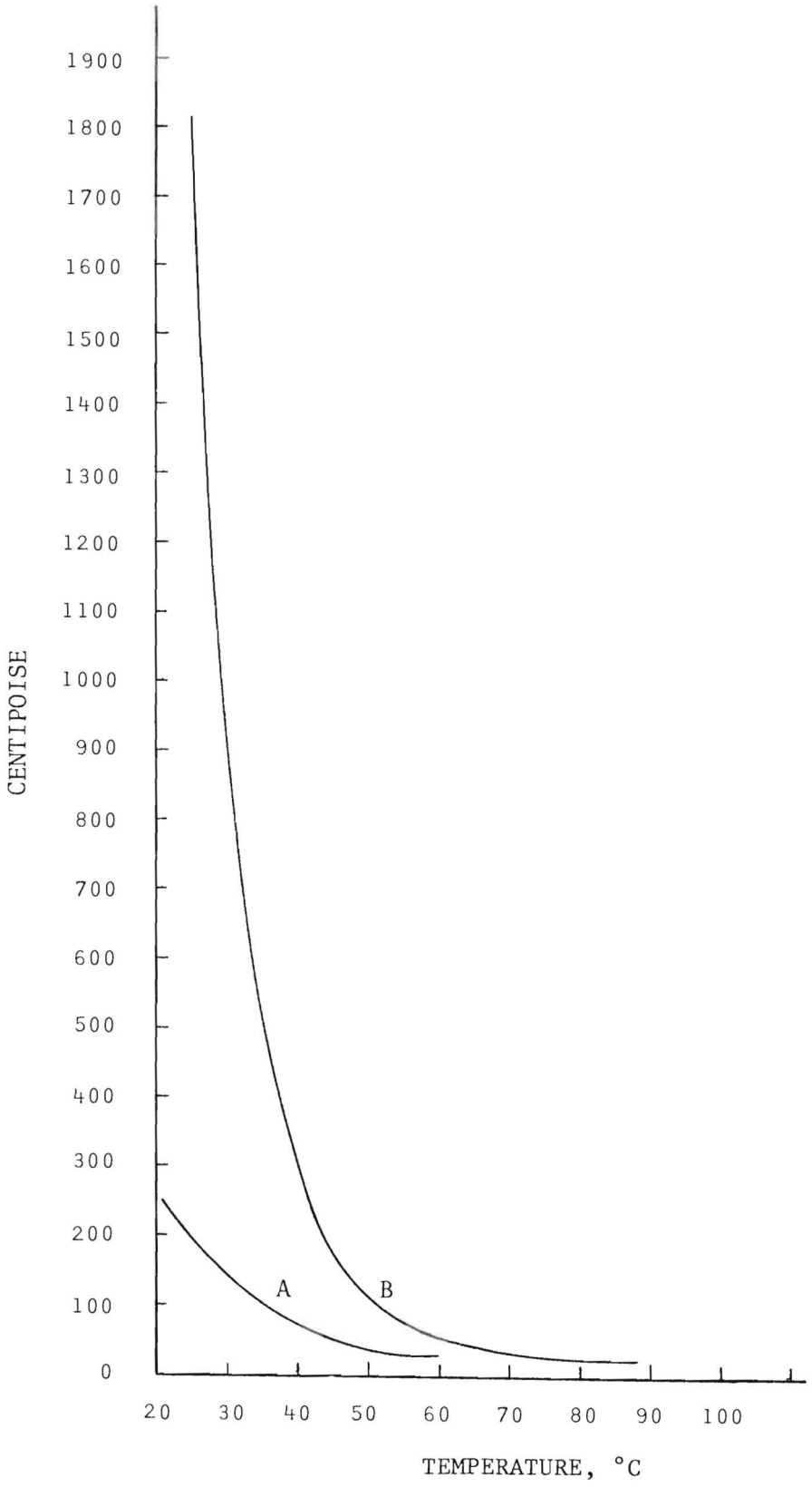

Figure 4. Vacuum stripped draft fan oil

A - Initial viscosity curve

B - Vacuum stripped viscosity curve

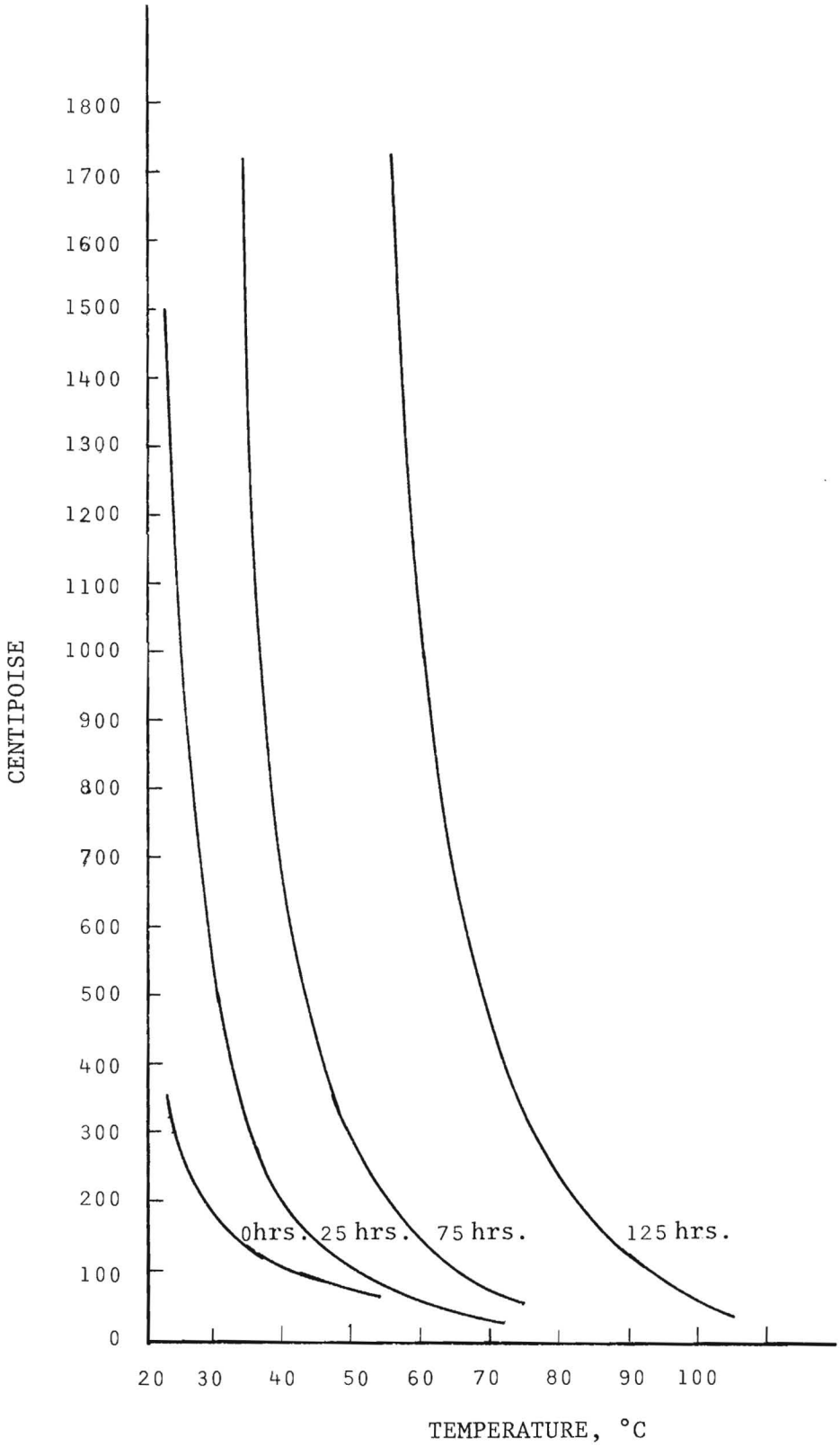

Figure 5. Effect of heating condenser oil at 110°C for different time periods on viscosity

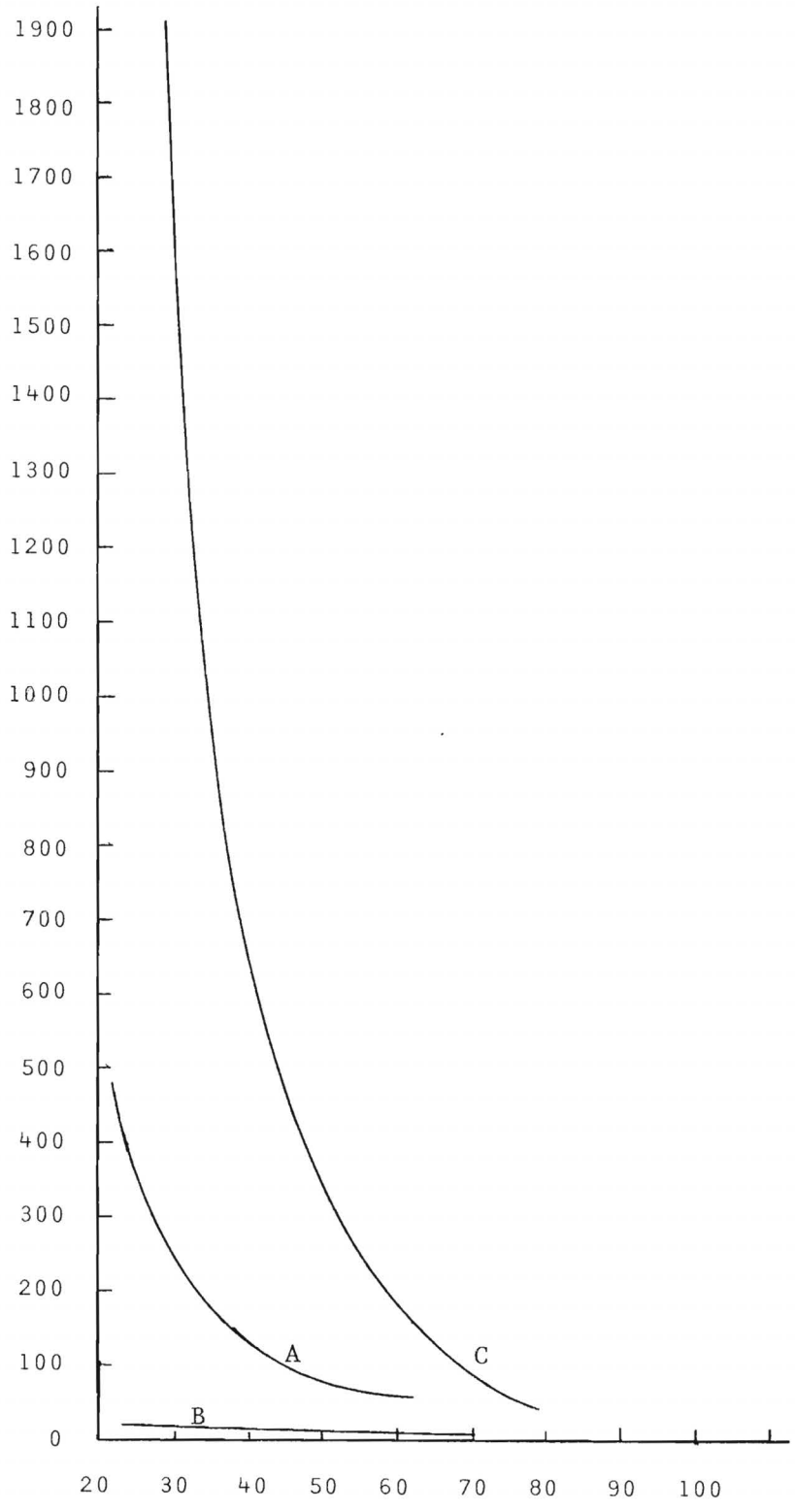

Figure 6. Viscosity curves for condenser oil (initial) and No. 2 and No. 6 fuel oils

A - Condenser oil

B - No. 2 Fuel oil

C - No. 6 Fuel oil

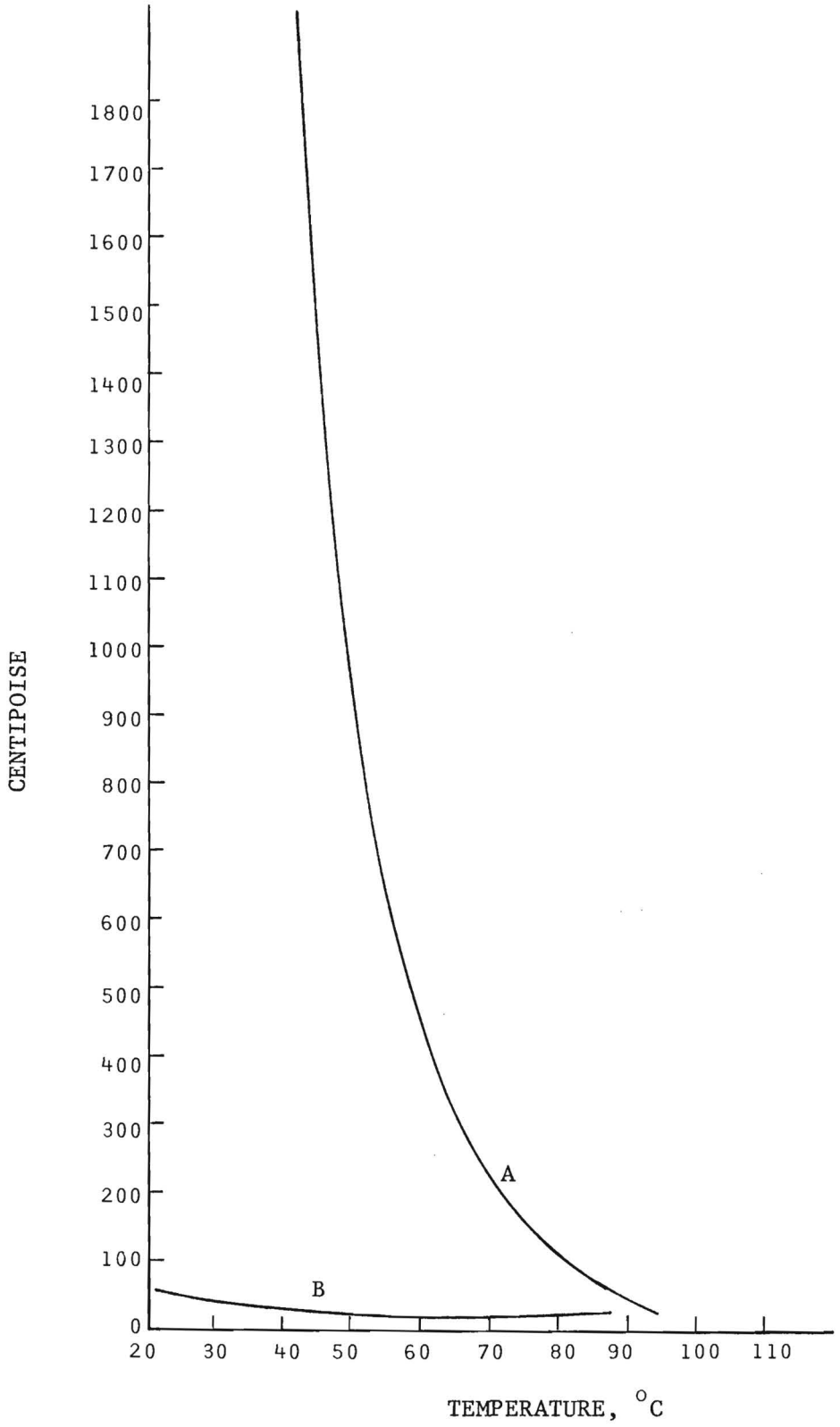

Figure 7. Viscosity of oils obtained May, 1977
A - Condenser oil
B - Draft fan oil

B. Partisil adsorption silica gel 5μ column. Solvent, 5-30% 2-propanol in isooctane, 20 min gradient, linear. Results: Resolution of only eight peaks.

C. Partisil PAC 5μ column. Solvent, 0-100% 2-propanol in isooctane, 30 min gradient 35 concave. Results: Resolution of 12 to 20 peaks. See Figure 8.

D. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in water, 30 min gradient 35 concave. Results: Resolution of 30-40 peaks. See Figure 9.

E. Partisil ODS 5μ column. Solvent, 10-100% acetonitrile in water, 10 to 40% with 20 minute hold, then 40% to 100% 35 concave gradient. Results: Resolution of 46-50 peaks. Total run time 60 minutes. See Figure 10.

From the above results, the resolution obtained with the conditions given in D above are very suitable for our survey chromatograms with the conditions in E being used for obtaining chromatograms of greater resolution.

Wavelength--The wavelengths 200, 220, 254, 280, 300, 320, 360 nm were selected and LC runs were made using constant conditions (E above) other than wavelength. The results were: (a) It was noted that many component responses appeared or disappeared with the change in wavelength; (b) no one wavelength was entirely satisfactory because at the shorter wavelengths of 200-220 nm excessive peak blending occured with high background levels which gave poorer peak resolution; (c) the longer wavelength of 300-360 nm produced sharply resolved peaks, but only a small total number of peaks actually appeared; (d) and the most satisfactory results for our purposes were obtained at 280 nm with 254 nm being the alternative choice. See Figures 11 through 15 for representative liquid chromatograms of this study with condenser wood oil using conditions in E above.

Solvent Gradient--The water-acetonitrile solvent system was found to be satisfactory for these wood oils. Water-methanol was tested but was unsatisfactory.

A. 10-100% acetonitrile solvent gradient with 35 concave instrument setting, 30 min long run with no solvent holds produced a short, fairly well resolved chromatogram with crowding of peaks during the last 25% of the run. See Figure 9.

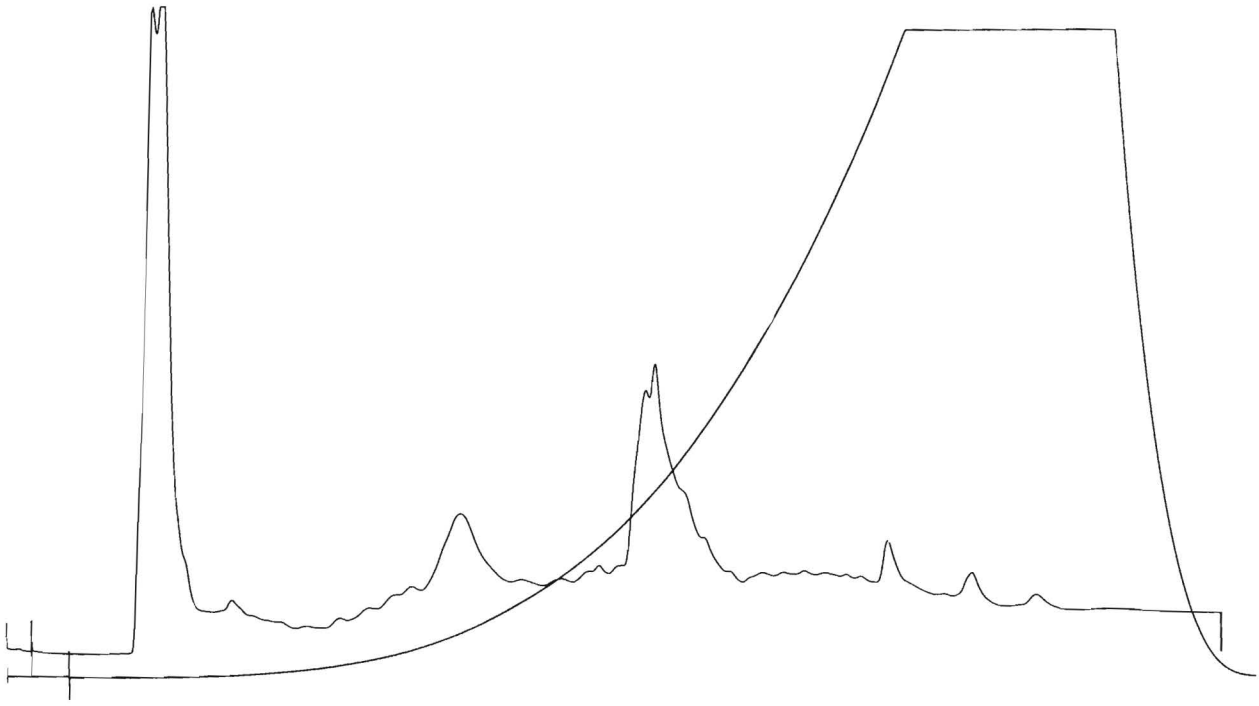

Figure 8. Liquid chromatogram of wood oil. Partisil PAC column with 0-100% solvent gradient of 2-propanol in iso-octane.

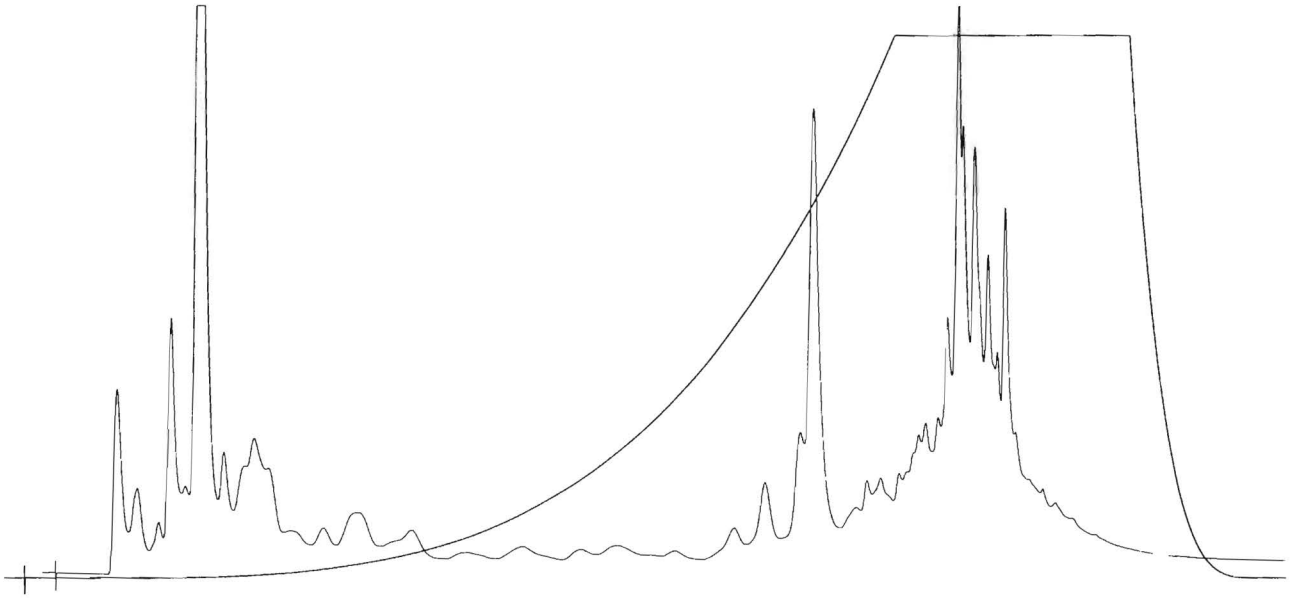

Figure 9. Liquid chromatogram of wood oil. Partisil PDS column with 10-100% solvent gradient of acetonitrile in water.

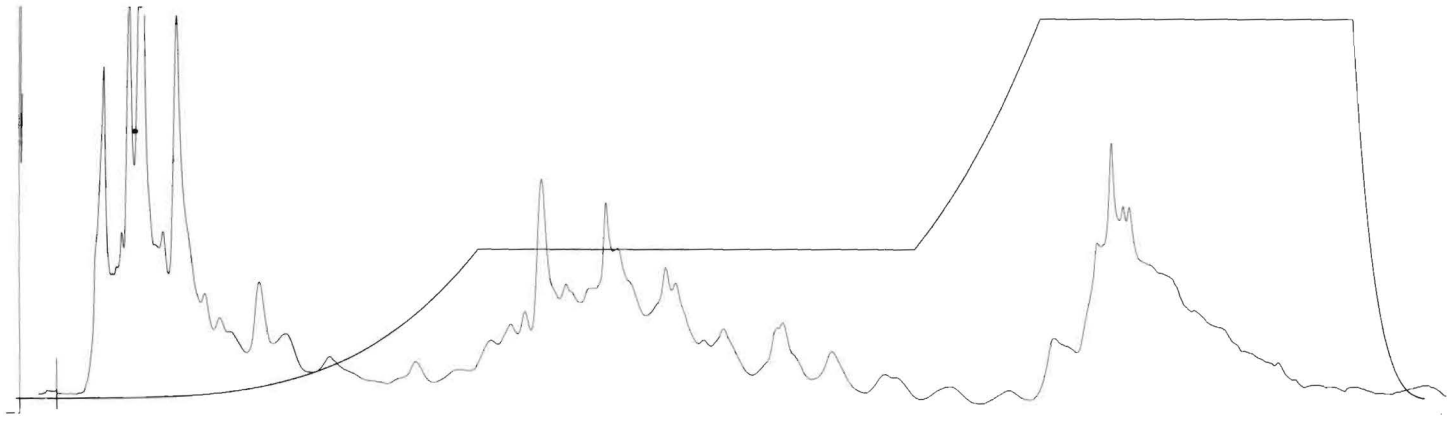

Figure 10. Liquid chromatogram of wood oil. Partisil ODS column with 10-100% solvent gradient of acetonitrile in water with 20 minute hold at 40% acetonitrile.

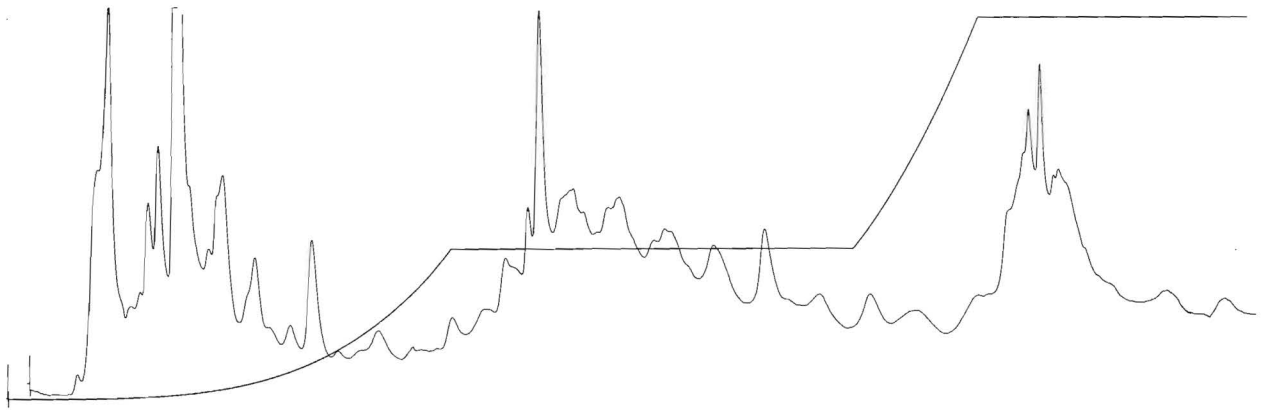

Figure 11. Liquid chromatogram of wood oil at 210 mm.

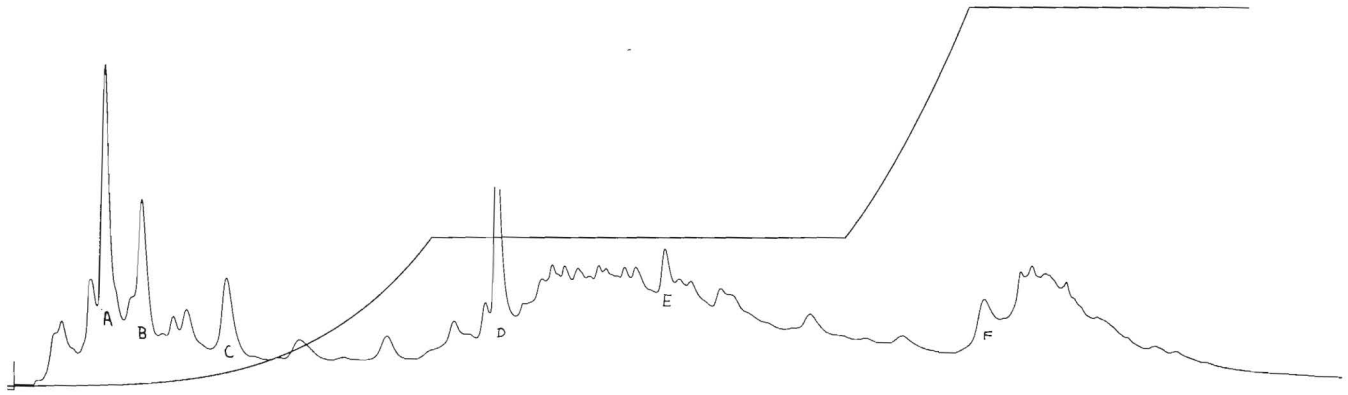

Figure 12. Liquid chromatogram of wood oil at 254 mm.

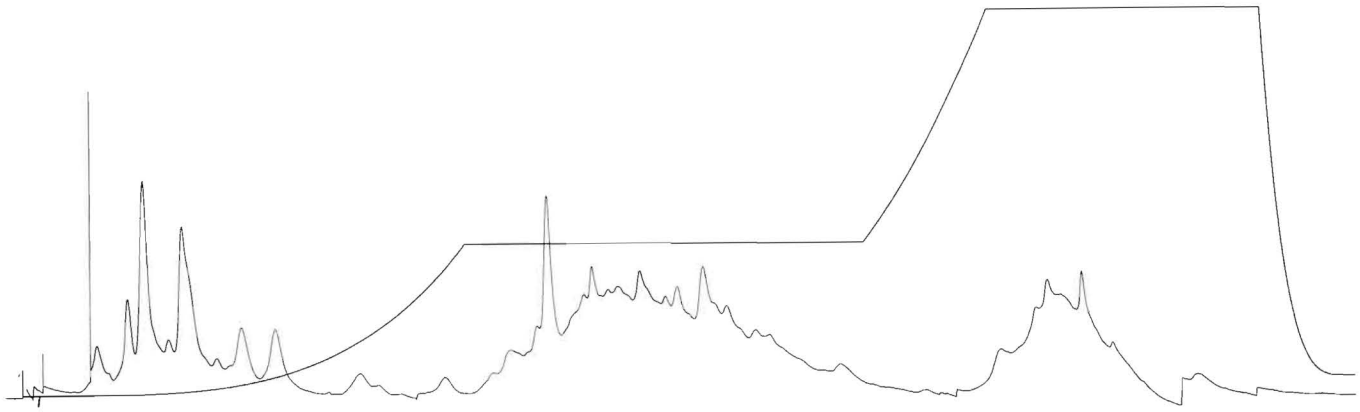

Figure 13. Liquid chromatogram of wood oil at 280 mm.

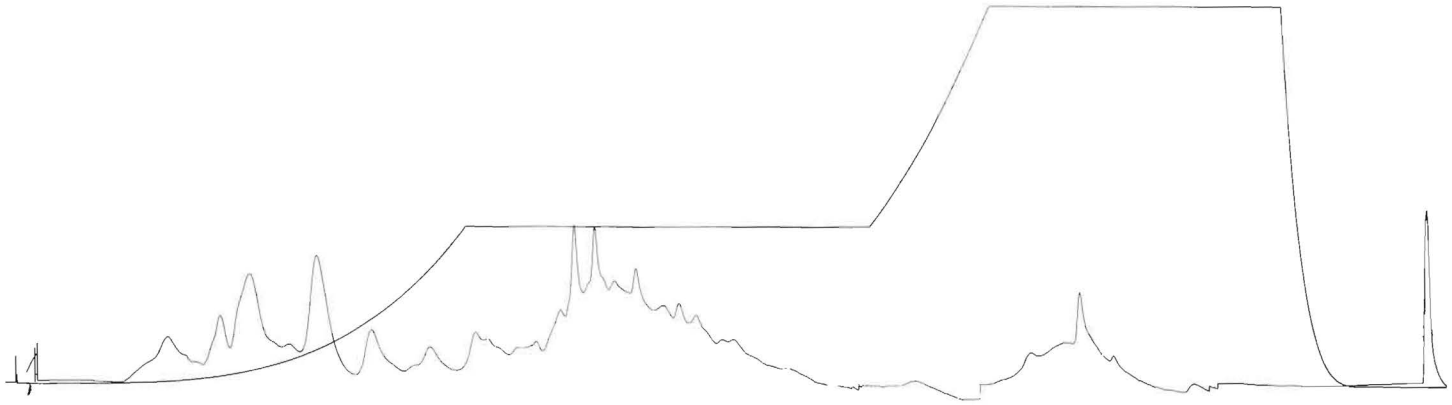

Figure 14. Liquid chromatogram of wood oil at 300mm.

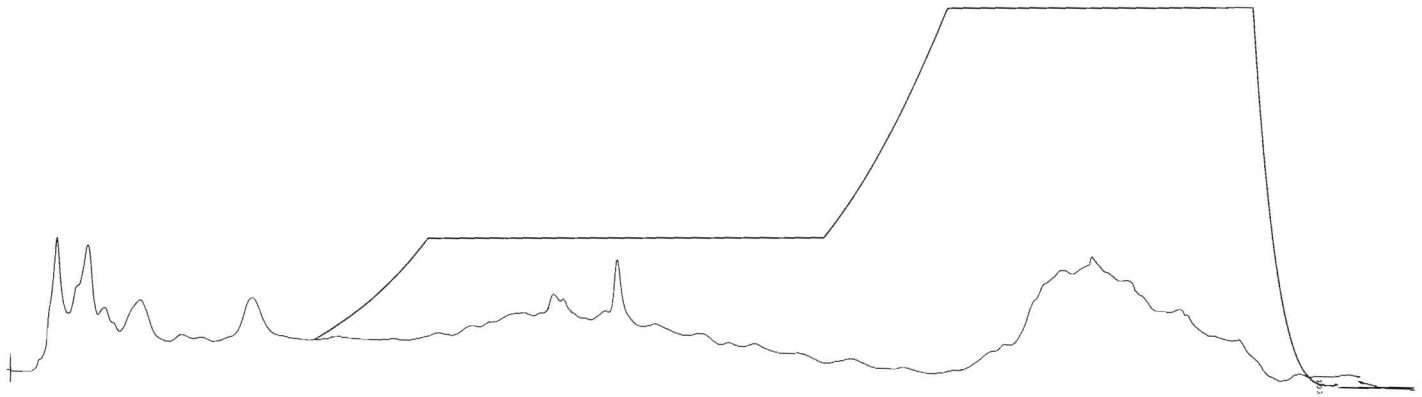

Figure 15. Liquid chromatogram of wood oil at 360 mm.

B. A 10-40% acetonitrile solvent gradient with 35 concave instrument setting, and solvent hold for 20 min, then to 100% for 10 min produced a very well resolved chromatogram in 60 min. This run produces typically 50 discernable peaks from the raw condenser oil test sample. See Figure 10.

C. A gradient with 5 min solvent holds at 20%, 30%, 40%, then 10 min at 100% did not produce a better resolved chromatogram than condition B. Condition B was selected as a standard gradient with condition A being used for survey scans.

Flow Rate--Liquid chromatograms were made using flow rates of 1 ml/min, 2 ml/min and 0.5 ml/min. A flow rate of 1 ml/min was selected because it produced the best resolution consistent with a practical time limitation of 1 hour per LC run.

Ultraviolet Spectral Scans--

In connection with the liquid chromatographic testing, ultraviolet spectral scans of some of the resolved components (peaks A, B, C, D, E and F of Figure 12) from the raw condenser oil were made as follows. A Tracor 970 wavelength LC detector was used in the stopped-flow mode to scan individual spectra of resolved components from 400 nm to 200 nm. The output was plotted on a Houston HR-100 X-Y recorder. An example of this method is shown in Figures 16 and 17. The results of this study explains why there is so much peak response variability in the LC wavelength response study above. This technique will possibly be used as an identification aid for components along with infrared spectra.

Liquid Chromatograms of Wood Oils--

Two sets of liquid chromatographic conditions were selected for obtaining liquid chromatograms of the oil samples. Survey liquid chromatograms are obtained with the conditions given in D and greater resolution liquid chromatograms are obtained with the conditions given in E in the above discussion on liquid chromatography. Survey liquid chromatograms are presented in Figures 18, 19, 20, and 21 for the condenser and draft fan wood oils obtained July, 1976, and the condenser and draft fan oils obtained May, 1977, respectively. An

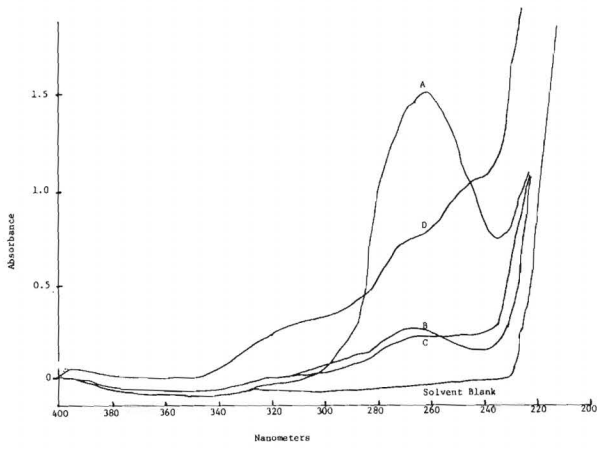

Figure 16. Ultraviolet spectra of peaks A thru D of wood oil from Figure 12.

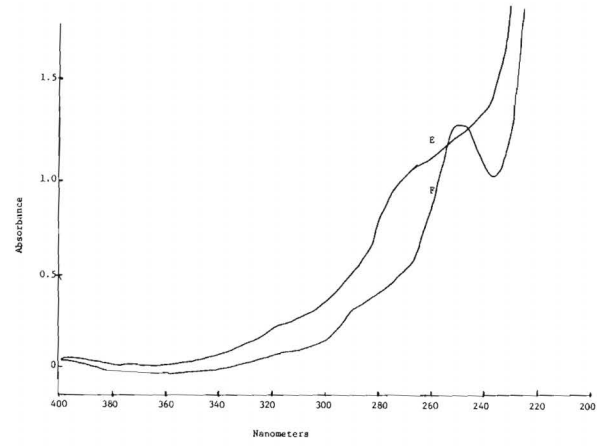

Figure 17. Ultraviolet spectra of peaks E thru F of wood oil from Figure 12.

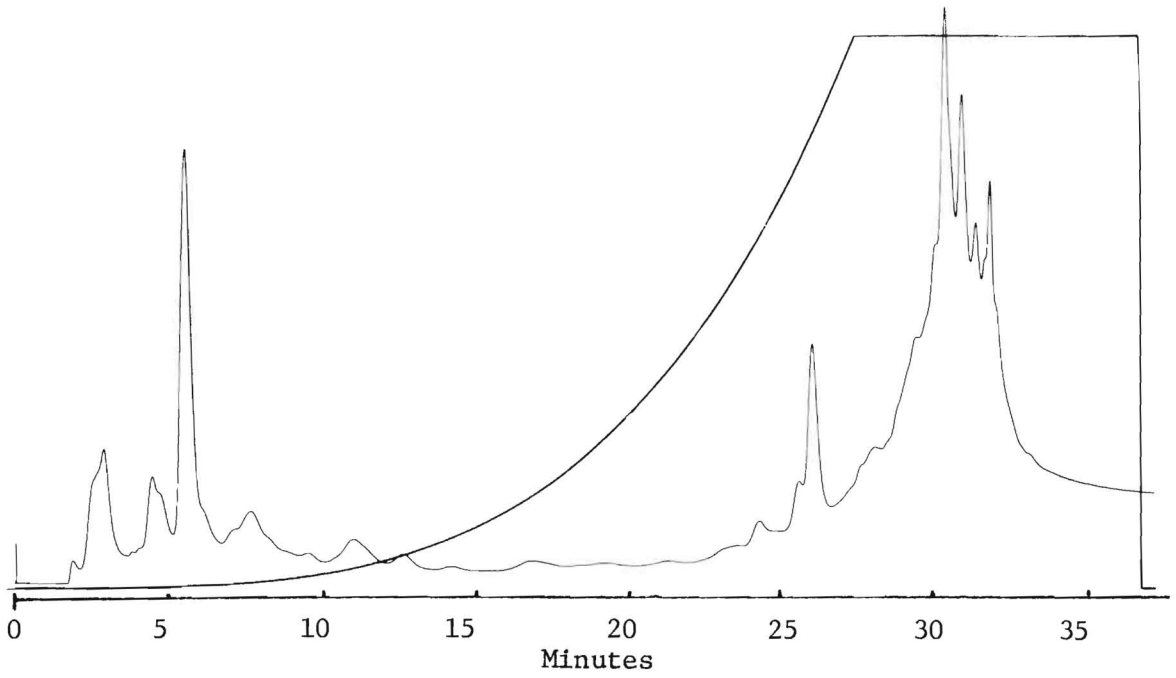

Figure 18. Survey liquid chromatogram of July, 1976 condenser wood oil.

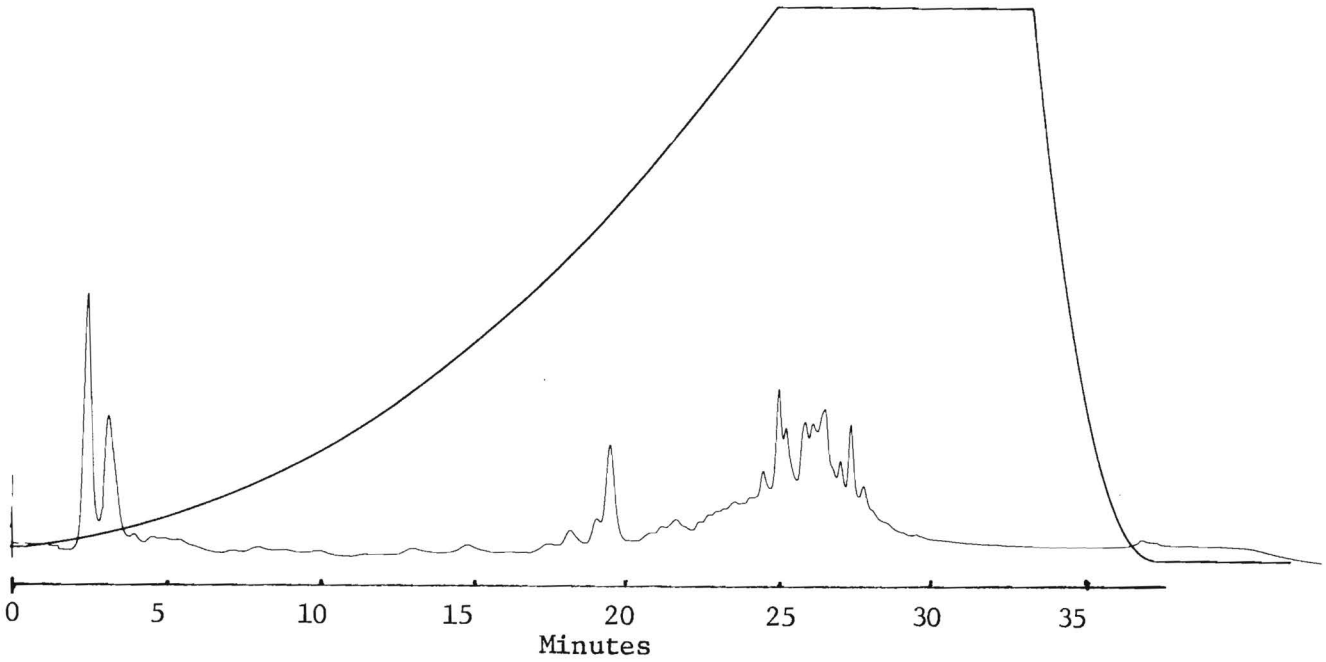

Figure 19. Survey liquid chromatogram of July, 1976 draft fan wood oil.

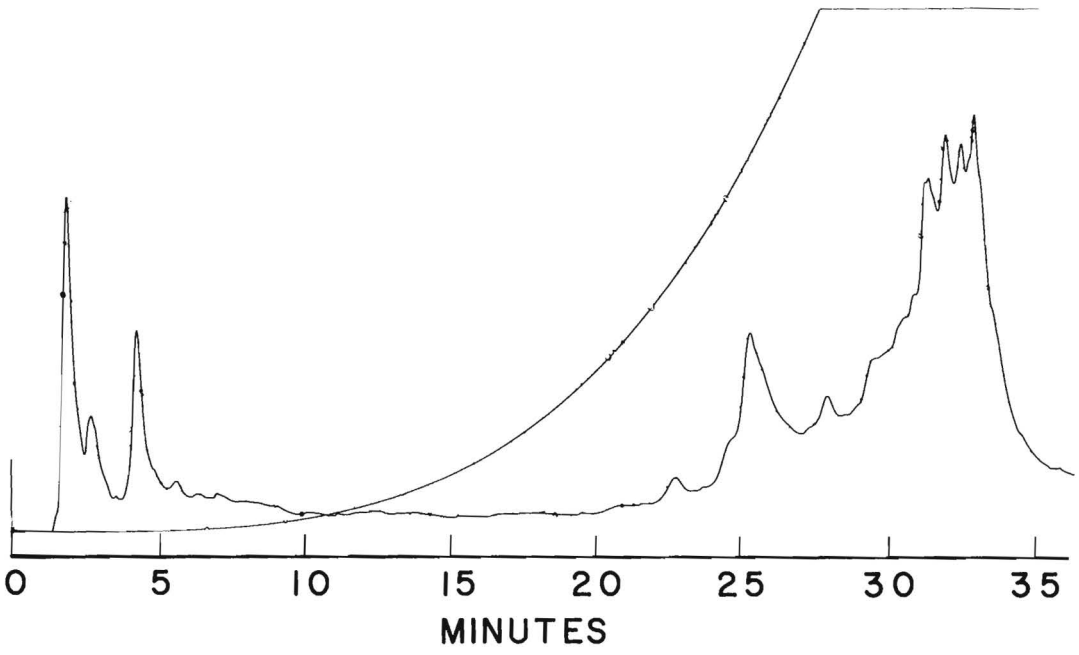

Figure 20. Survey liquid chromatogram of May, 1977 condenser wood oil.

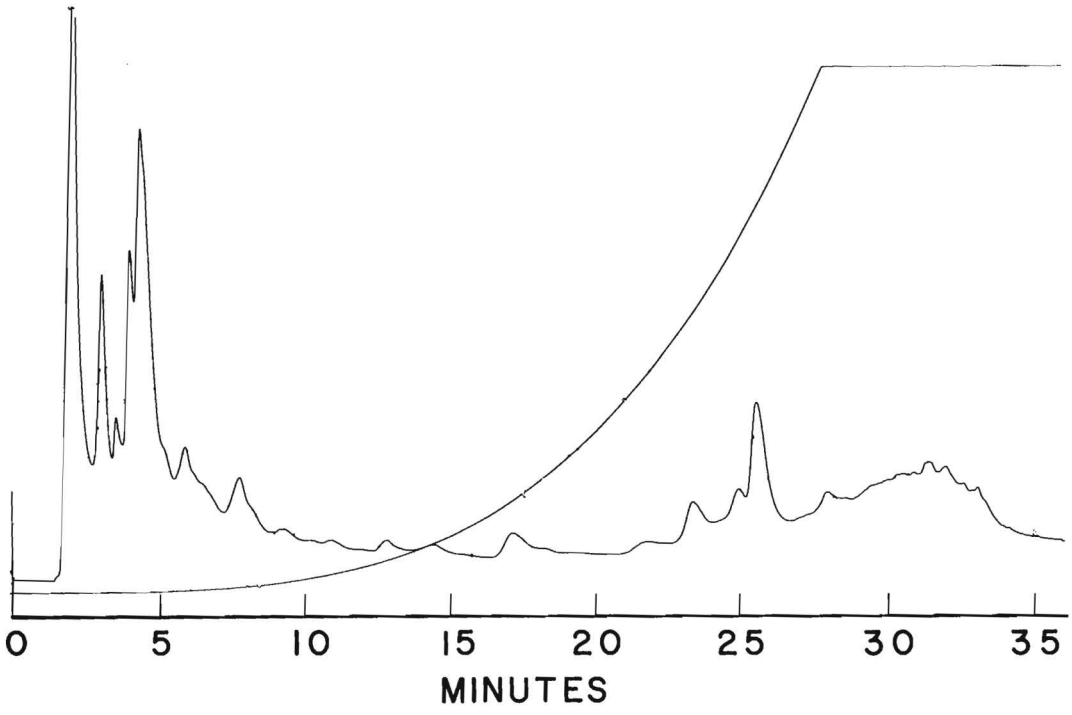

Figure 21. Survey liquid chromatogram of May, 1977 draft fan wood oil.

examination of these chromatograms shows that all of the samples have a large number of components and that each chromatogram has distinctive features. From other work with gas chromatography of the oils, it is quite evident that complete resolution of the oil samples by liquid chromatography has not been obtained with the conditions being employed. The results obtained with these conditions are however adequate for current needs. Efforts will continue to develop better liquid chromatographic conditions for characterization of these types of oils.

Molecular Weight Determinations of Wood Oils by LC--

The results from the processing of wood oils from pyrolysis of wood, particularly when subjected to heat, indicate that reactions occur which produce higher molecular weight components. It is also desirable to have information on the molecular weight distribution of the raw wood oils. In an attempt to obtain some information which would be indicative of the molecular weight range of the oils and fractions of oil, the newly available size exclusion liquid chromatographic columns of silica gel with narrow pore size distribution were utilized. The column selected was a 25 cm column of DuPont SE-60 controlled size deactivated silica which has a molecular weight range of linear operation of approximately 100 to 800 $\bar{M}w$. Polystyrene standards of 800, 2200 and 9000 were obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania. Benzene, molecular weight 78, was also used. In these LC runs, the solvent was tetrahydrofuran and the UV detector was set at 280 nm. The average molecular weights of raw wood oils and some oil fractions were obtained. In addition, the still bottoms from a commercial distillation of a wood oil was tested. The preliminary results from this initial work are given in Table 6.

Gas Chromatographic Procedures

Gas chromatography (GC) offers an excellent technique for analyzing complex mixtures of organic compounds. The apparent disadvantage in analyzing wood oils produced by pyrolysis GC is the heat sensitivity of some components in wood oils and the possible effect of the heat on these components during GC analysis. Recognizing this possible constraint, GC should be useful for analysis for fractions containing more volatile components and for water soluble components. In addition, it was considered appropriate to do some preliminary analysis of

TABLE 6. PRELIMINARY AVERAGE MOLECULAR WEIGHT DETERMINATIONS

Sample Description	$\bar{M}w$	Comment
Raw Condenser Oil	160	-
Raw Draft Fan Oil	150	-
Still Bottoms from Atmospheric Distilled Oil	150	-
Vacuum Spinning Distillation Band Fract. 1-4	>100	-
Fract. 8	80 and 120	Two Main Components
Fract. 12	150	-
Still Bottoms Steam Distilled Oil	150	-
Still Bottoms from Commercially Distilled Oil*	112 - 9000	Broad $\bar{M}w$ Distribution

* Obtained from Tech-Air Corporation

the raw wood oils because of the powerful analytical capability of GC. The instrumentsused were a Perkin Elmer Model 900 with a flame ionization detector with dual column and temperature programmed capability, and a Perkin Elmer Model 990 with thermal conductivity detector, dual column, and isothermal oven.

The objectives of this gas chromatographic work are to be able to resolve the low molecular weight components in the aqueous phases of various distilled fractions, to resolve the more volatile components of the oils and fractions of oil, and to analyze the higher molecular weight components of the relatively water-free wood oils and fractions obtained from the oils. To date, two columns were selected from several GC trial runs with the raw condenser oil and a distilled aqueous fraction. The list of columns and conditions that have been tried are given below.

Initial Conditions: P.E. 900 FID detector. Carrier gas, N_2 at 20 ml/min temperature program as shown.
P.E. 990 T.C. detector. Helium carrier gas at 20 ml/min; isothermal oven.
Samples tested were raw condenser oil and aqueous distillation fraction.

Column 1. Porapak Q, 9' x 1/8," with 1' x 1/8" Porapak Q precolumn to retain and prevent the heavy organics from entering the main column. Oven 120°C, injector 200°C, thermal conductivity detector 225 ma, Helium carrier at 20 ml/min. Results: The determination of water, lower alcohols, formaldehyde and acetone was accomplished.

Column 2. 3% Poly-m-phenoxylene on 80/100 Chrom P DMCS, 6' x 1/8." Injector 250°C, manifold 250°C, oven 130°-200°C @ 8°/min. FID, N_2 at 20 ml/min. Results: moderate resolution of sample, 18 peaks, from raw oil.

Column 3. 10% Dow Corning High Vacuum Grease on 80/100 AWFB-DMCS 10' x 1/8." Injector 340°C, oven 150°-350°C @ 10°/min FID, N_2 20 ml/min. Results: 48 peaks minimum resolution from raw oil.

Column 4. 1% Polyphenylether (6 ring) on 80/100 AWFB-DMCS 3' x 1/8." Injector 250°C, manifold 250°C, oven 130°C @ 10°/min FID, N_2 20 ml/min. Results: moderate resolution of sample, 23 peaks from raw oil.

Representative GC chromatograms of the July, 1976, raw condenser oil sample and of fractions obtained by steam distillation, simple vacuum distillation and vacuum fractionation with a spinning band column are given in Figures 22 through 33. Column 3 and the conditions listed above with column 3 were used for these chromatograms with a total retention time of about 30 minutes.

DISTILLATION OF WOOD OILS

Distillation offers a possible method for processing and refining wood oils obtained by pyrolysis and other similar produced oils to yield more desirable and useful products, and thereby, increasing the economic value of the oils. With this objective, a number of wood oil samples were distilled under a variety of conditions as a part of this study. Details of these distillations are given below.

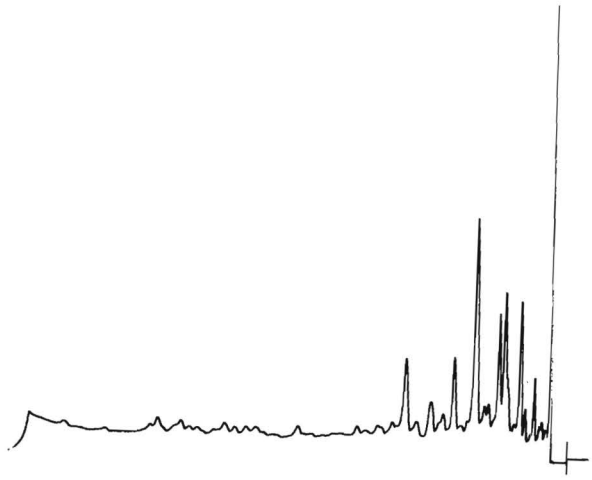

Figure 22. Gas Chromatogram of July, 1976 condenser wood oil.

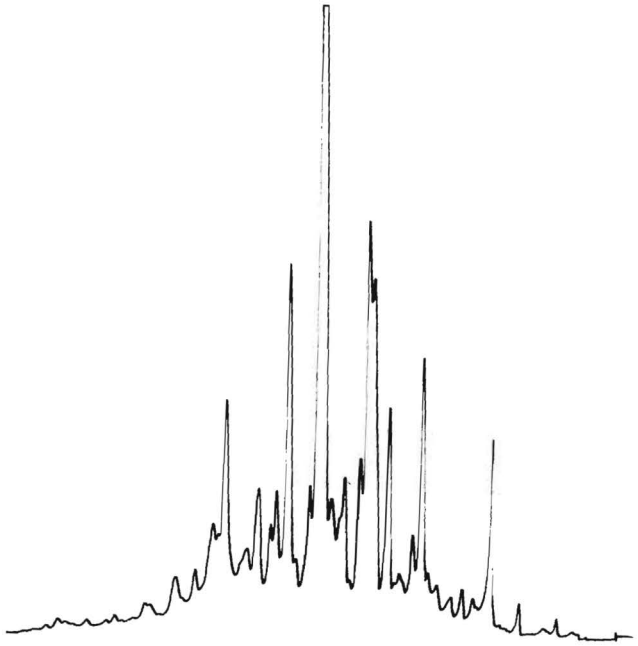

Figure 23. Gas chromatogram of first organic fraction from steam distillation of wood oil.

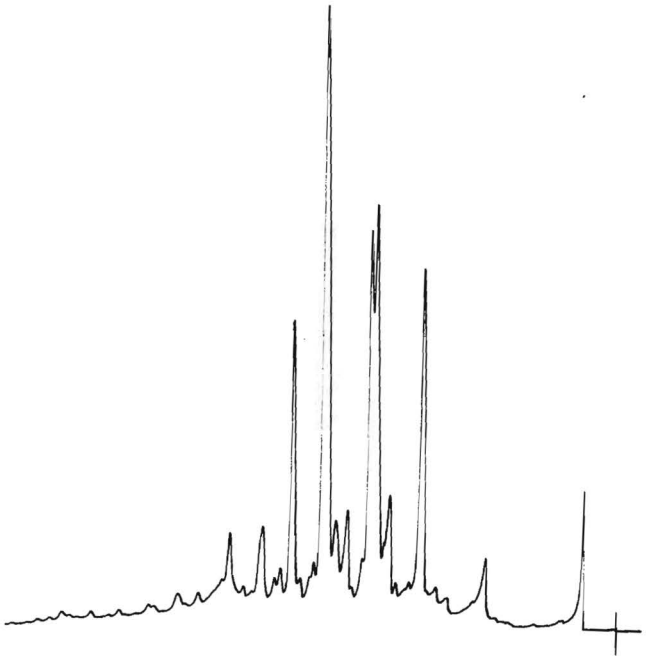

Figure 24. Gas chromatogram of second organic fraction from steam distillation of wood oil.

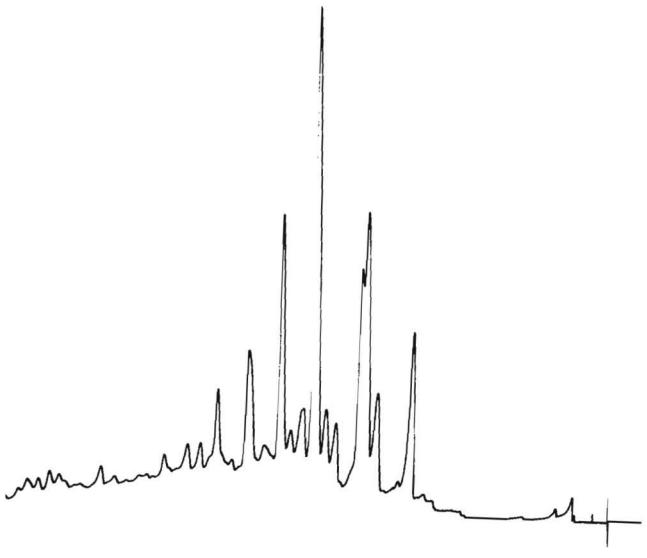

Figure 25. Gas chromatogram of third organic fraction from steam distillation of wood oil.

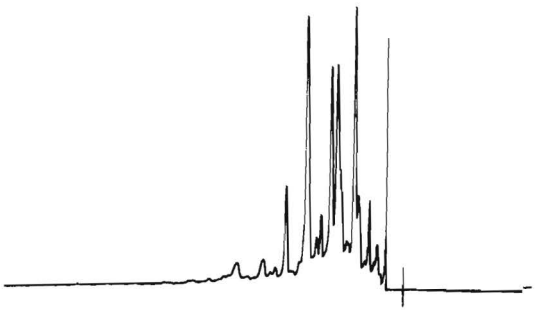

Figure 26. Gas chromatogram of first fraction from simple vacuum distillation of wood oil.

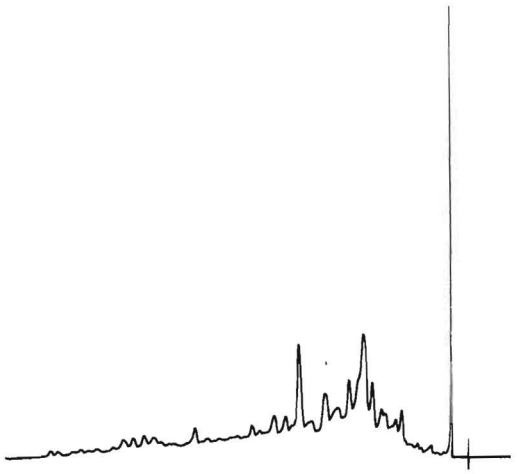

Figure 27. Gas chromatogram of third fraction from simple vacuum distillation of wood oil.

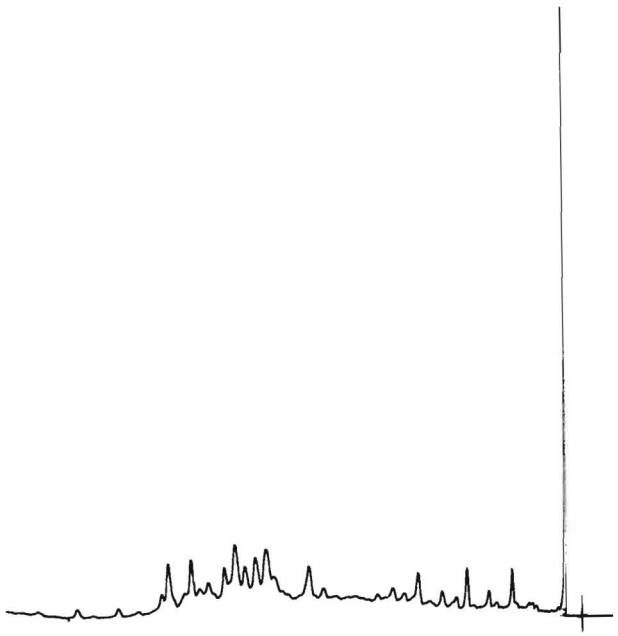

Figure 28. Gas chromatogram of fourth fraction from simple vacuum distillation of wood oil.

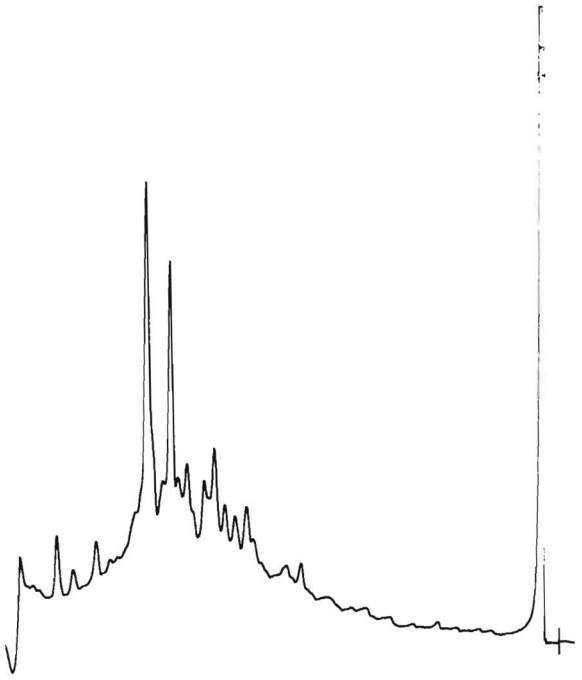

Figure 29. Gas chromatogram of flask residue from simple vacuum distillation of wood oil.

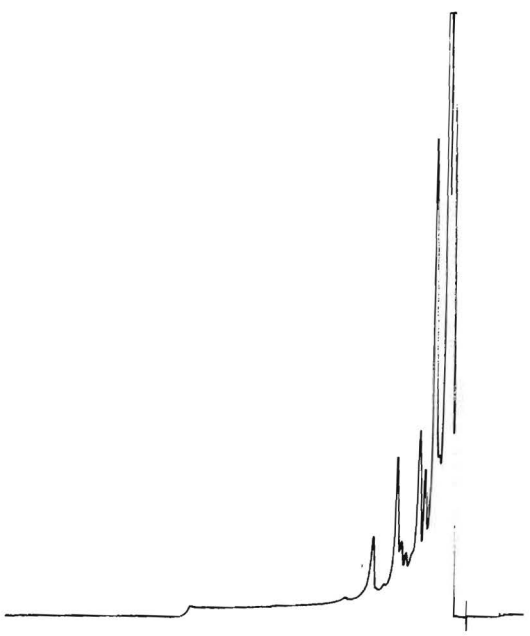

Figure 30. Gas chromatogram of aqueous phase from simple vacuum distillation of wood oil.

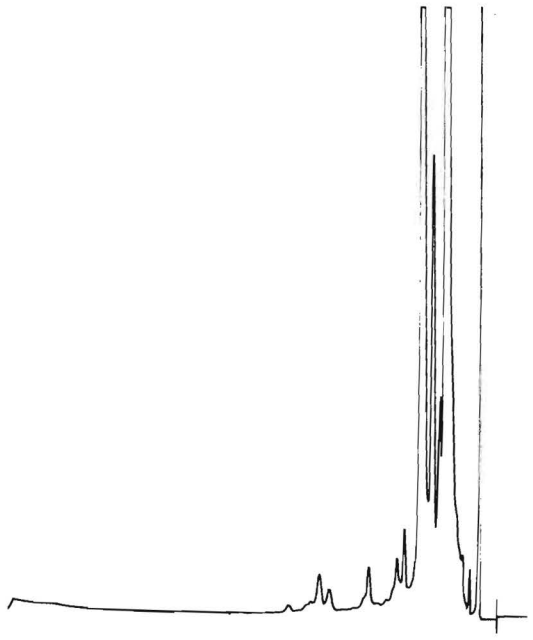

Figure 31. Gas chromatogram of fraction one from vacuum distillation of wood oil with spinning band column.

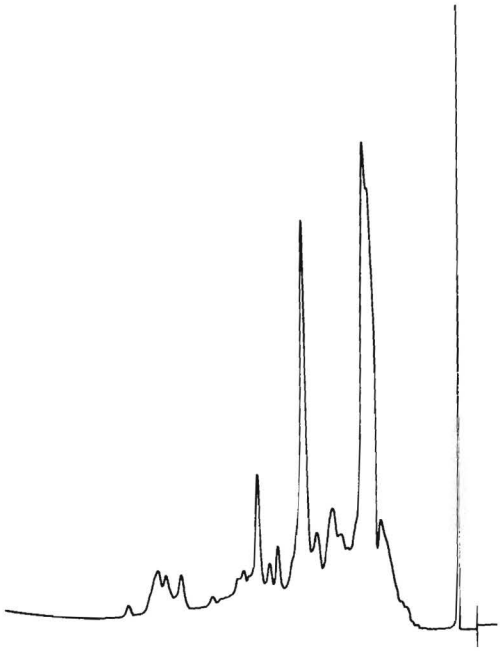

Figure 32. Gas chromatogram of fraction five from vacuum distillation of wood oil with spinning band column.

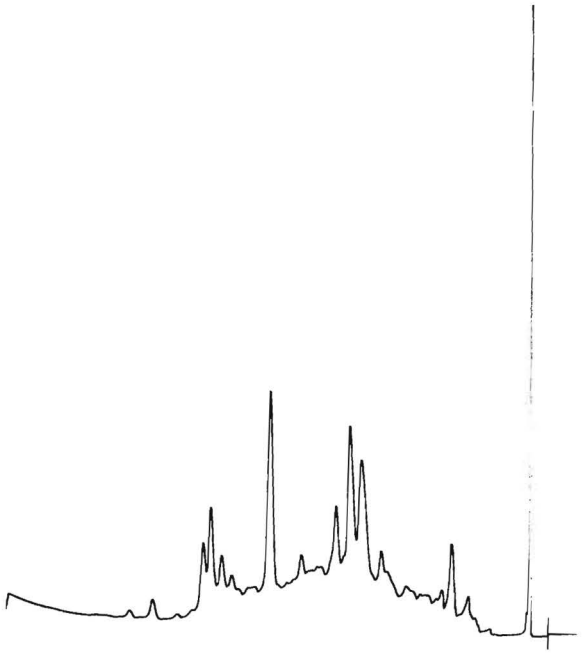

Figure 33. Gas chromatogram of fraction nine from vacuum distillation of wood oil with spinning band column.

Distillation at Atmospheric Pressure

A sample of condenser wood oil, 183 g, was distilled at atmospheric pressure in a simple distillation apparatus. Initially, the distillate consisted mainly of an aqueous phase with some oil droplets. Most of the aqueous distillate was obtained over the temperature range of 95°-125°C. Between 125°C and 190°C, the distillate was mostly heavy oil with some water and light oil. Starting at 190°C head temperature and up to 230°C, the distillate was mainly light oil. Some water droplets also distilled in this temperature range. After 120 ml of distillate had been collected, the head temperature began to drop. The distillation was discontinued when the head temperature dropped to 150°C. At this point, there was no distillate and the material in the flask has just started to give off a gaseous phase. The heavier oily phase represented 60% of the total oil distillate, and the lighter oily phase, 40%. The data on the distillation is given in Table 7. The recovery of 93.2% indicates that some gases were possibly lost during the distillation. No provision was made for collecting any gases during the distillation.

TABLE 7. ATMOSPHERIC DISTILLATION DATA

Fraction	Head Temperature, °C	Yield, %
Aqueous Phase*	95°-125°	20.7
Heavy Oil	105°-190°	28.4
Light Oil	190°-230°	19.1
Residue†		25.0
		93.2

* Contained 6.2% organic material as determined by gas chromatography.
† The residue solidified on cooling to room temperature.

The analytical data on the oil phases and the residue are presented in Table 8.

TABLE 8. ANALYTICAL DATA--ATMOSPHERIC DISTILLATION FRACTIONS

Property	Light Oil	Heavy Oil	Residue
Density, g/ml	0.9988	1.0423	--
pH	3.5	2.9	--
Acid No., mg KOH/g	52	17.8	--
Elemental Analysis			
Carbon %	67.4	74.0	60.1
Hydrogen %	7.5	8.2	2.9
Nitrogen %	0.1	0.7	0.8

Survey liquid chromatograms the heavy and light organic phases are presented in Figures 34 and 35.

Vacuum Distillation

Condenser Oil--

A sample of July, 1976, condenser oil was distilled in a simple vacuum distillation apparatus at 0.2-0.4 mm Hg pressure with dry-ice and liquid nitrogen traps for recovery of volatile material. The aqueous phase containing light organics was obtained before the head temperature reached 43°C head temperature, the distillation was discontinued as the material in the flask was becoming more viscous and appeared to be approaching a decomposition stage. The vacuum distillation data are presented in Table 9.

TABLE 9. VACUUM DISTILLATION DATA

Fraction	Head Temperature, °C	Yield,%
Aqueous and light organics phase*	Ambient to 43°	23.1
1	43°-125°	17.6
2	125°-140°	2.1
3	140°-180°	18.5
4	180°-190°	2.6
Residue	--	32.4
		96.3

* Contained 46% organic material as determined by gas chromatography.

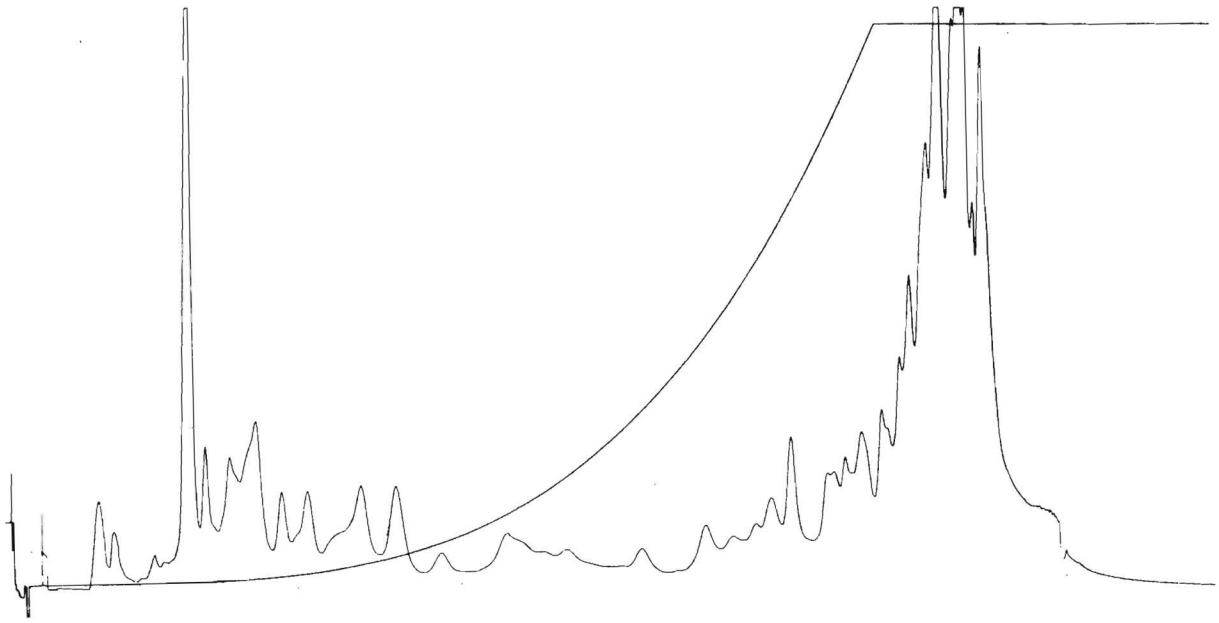

Figure 34. Survey liquid chromatogram of heavy organic oil from atmospheric distillation.

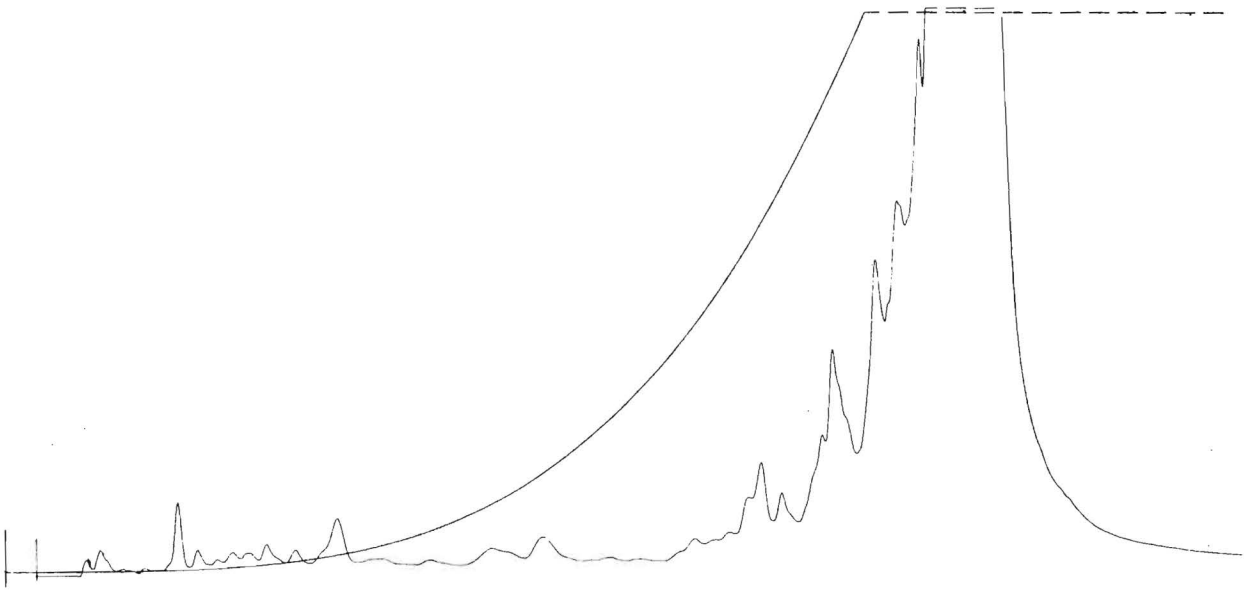

Figure 35. Survey liquid chromatogram of light organic oil from atmospheric distillation.

The oil fractions one through four were combined to obtain a sample of oil for fractionation under vacuum with a spinning band column. Analytical data on the combined oil fractions are given in Table 10.

TABLE 10. ANALYTICAL DATA--VACUUM DISTILLATION

Property	Combined Fractions 1-4
Density, g/ml	1.091
pH	2.8
Acid No., mg KOH/g	59.6
Heating value, cal/g	6,092
Btu/lb	10,964
Elemental Analysis	
Carbon, %	62.7
Hydrogen,%	7.7
Nitrogen, %	0.3

A survey liquid chromatogram of the combined fractions is presented in Figure 36.

Draft Fan Oil--

A sample of the refrigerated July, 1976, draft fan oil, which had been vacuum stripped to remove the water, was distilled in a simple vacuum apparatus at ~ 0.5 mm mercury pressure. Dry ice and liquid nitrogen traps were used to recover volatile material. The first distillate was obtained at a head temperature of 48°C. The head temperature rose gradually during the distillation to 122°C maximum at the end of the distillation. The flask temperature was held to a maximum of 150°C. Toward the end of the distillation, the head temperature reached a maximum of 122°C and then started to drop. The distillation was discontinued at this point. Condensate was collected in the first dry ice cold trap only. The data on the distillation is given in Table 11.

Survey liquid chromatograms of the cold trap sample, fractions one through five and of the remaining flask material are presented in Figures 37 through 43, respectively, for comparison.

TABLE 11. VACUUM DISTILLATION OF DRAFT FAN OIL

Fraction	Flask Temperature, °C	Head Temperature, °C	Yield, %
1	23-85°	48-65°	8.46
2	85-100°	65-72°	8.98
3	100-110°	72-86°	6.37
4	110-125°	86-105°	9.29
5	125-150°	105-122°	10.65
Cold trap		Ambient	7.52*
Material in flask		-	52.8
		Total	104.1*

* Most of the material in the cold trap was water. Since the total is over 100% a portion of the cold trap condensate could be due to water vapor from leaks.

Vacuum Spinning Band Distillation

A sample of the combined oil fractions from the vacuum distillation of the condenser oil described above was distilled in a Nester-Faust spinning band distillation column at 0.2-0.4 mm pressure mercury with liquid nitrogen traps for recovery of volatile material. The distillation data are given in Table 12 below.

TABLE 12. SPINNING BAND DISTILLATION DATA

Fraction	Head Temperature, °C	Yield, %
1	35-48°	8.0
2	48-58°	14.6
3	58-60°	8.5
4	60-68°	2.1
5	68-74°	6.9
6	74-82°	6.0
7	82-88°	4.6
8	88-98°	2.8
9	98-105°	5.5
Flask Residue	--	30.0
Trap Material	--	7.8
	Total	96.8

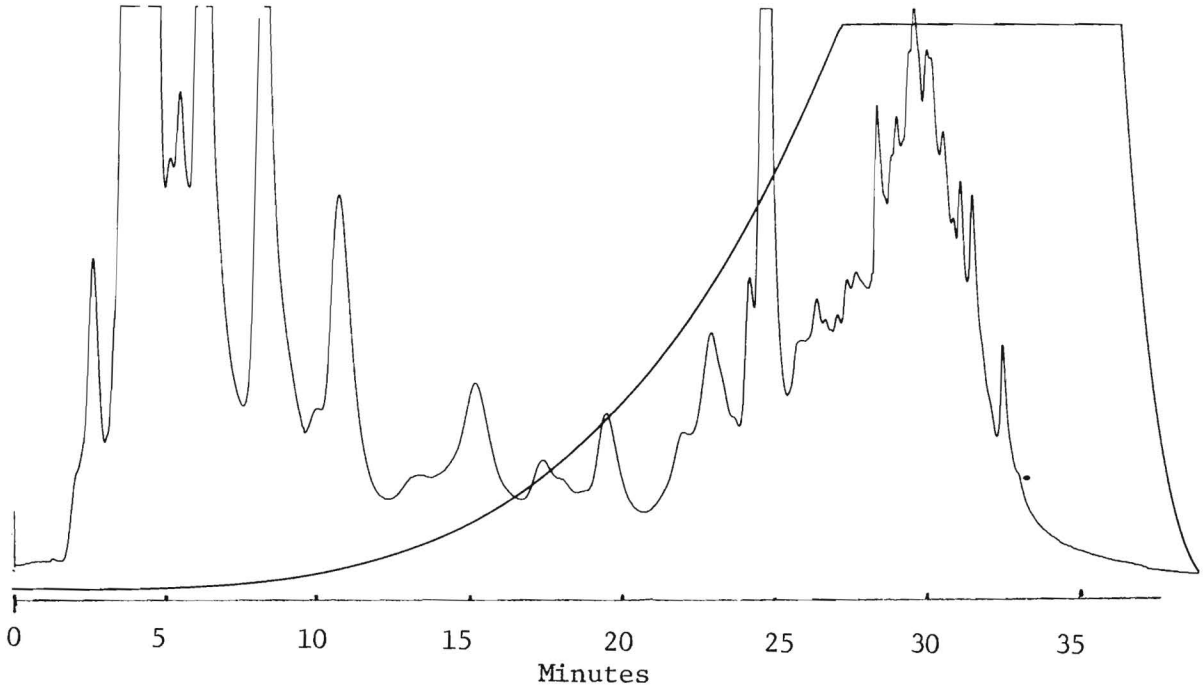

Figure 36. Survey liquid chromatogram of combined fractions from vacuum distillation.

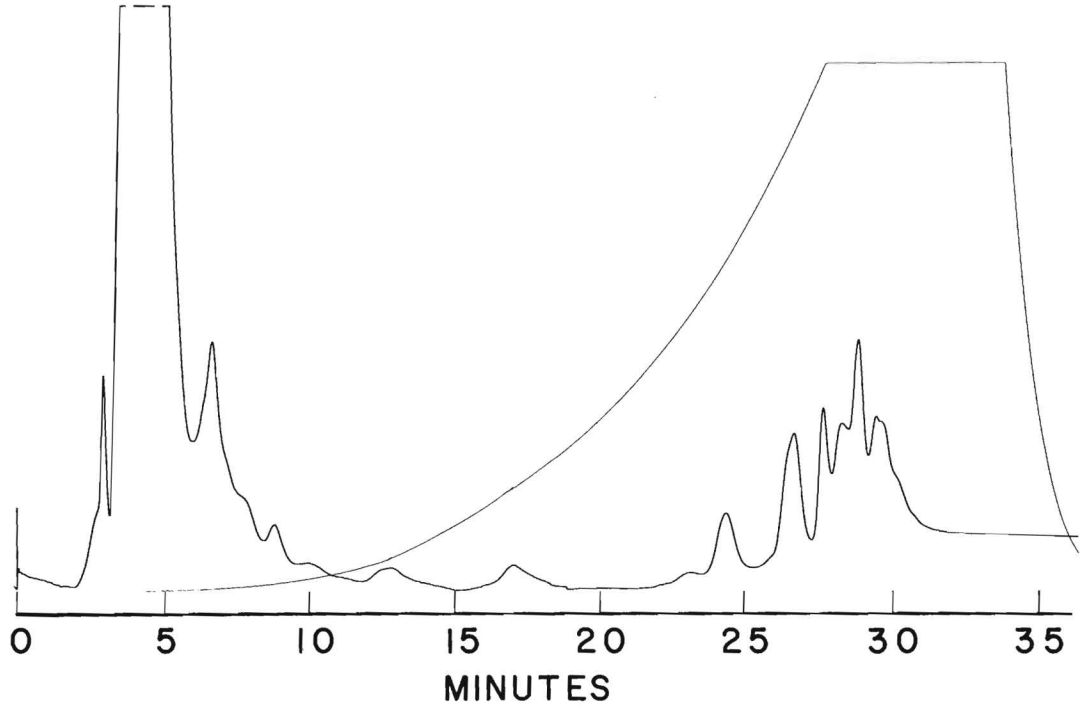

Figure 37. Survey liquid chromatogram of cold trap sample from vacuum distillation of draft fan wood oil.

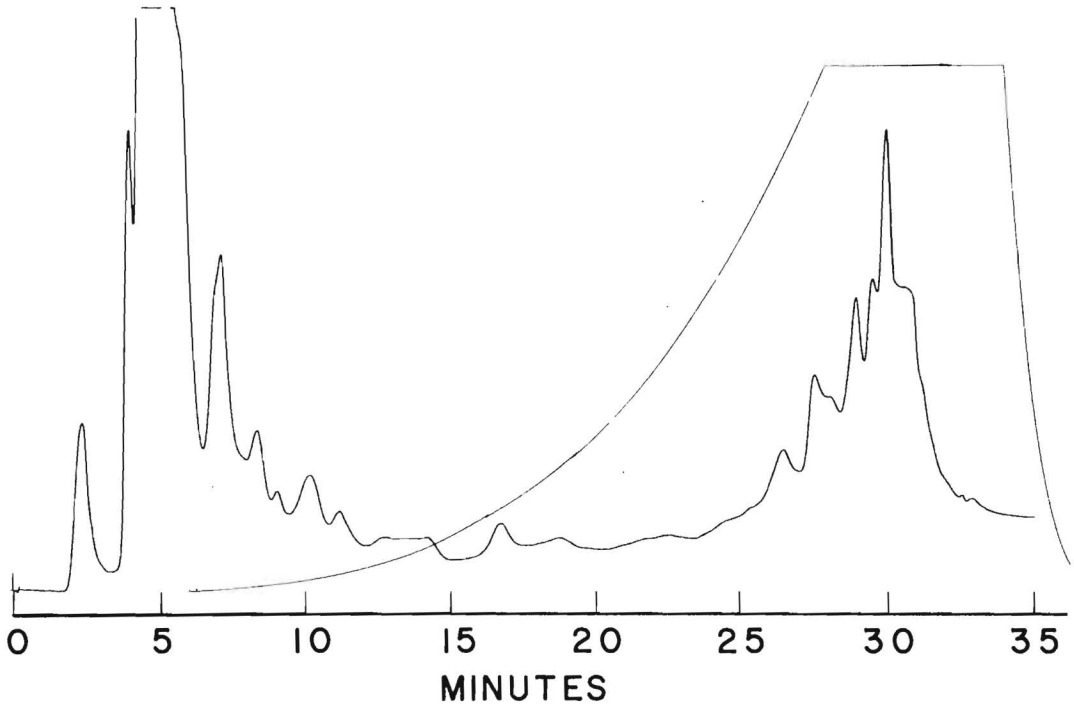

Figure 38. Survey liquid chromatogram of fraction one from vacuum distillation of draft fan wood oil.

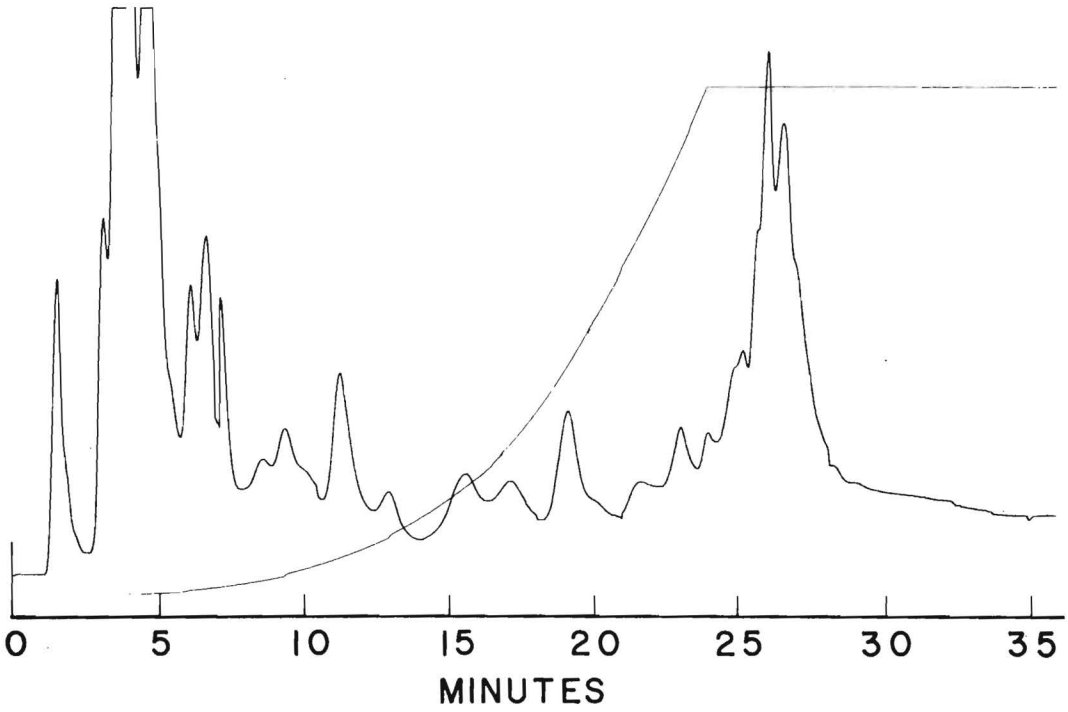

Figure 39. Survey liquid chromatogram of fraction two from vacuum distillation of draft fan wood oil.

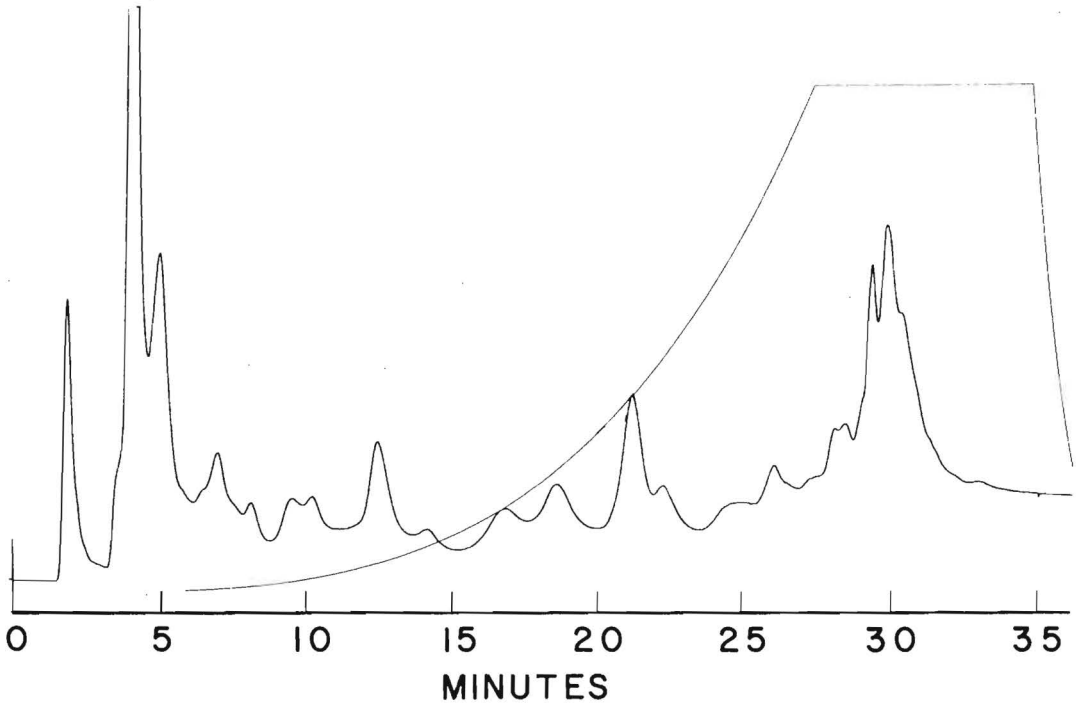

Figure 40. Survey liquid chromatogram of fraction three from vacuum distillation of draft fan wood oil.

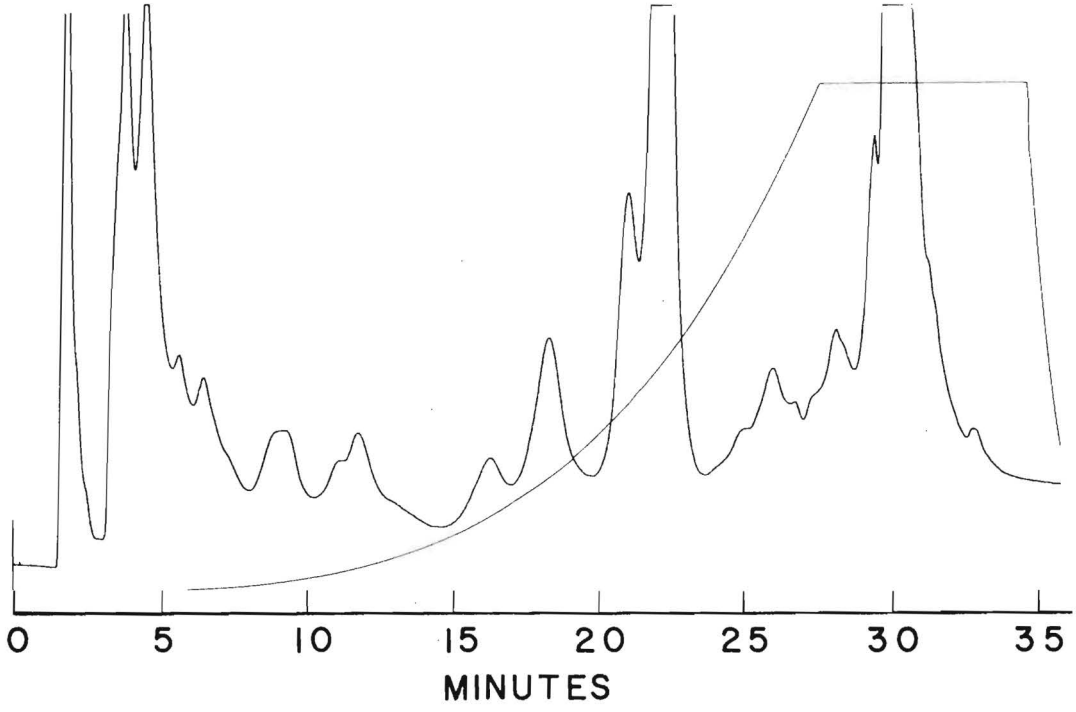

Figure 41. Survey liquid chromatogram of fraction four from vacuum distillation of draft fan wood oil.

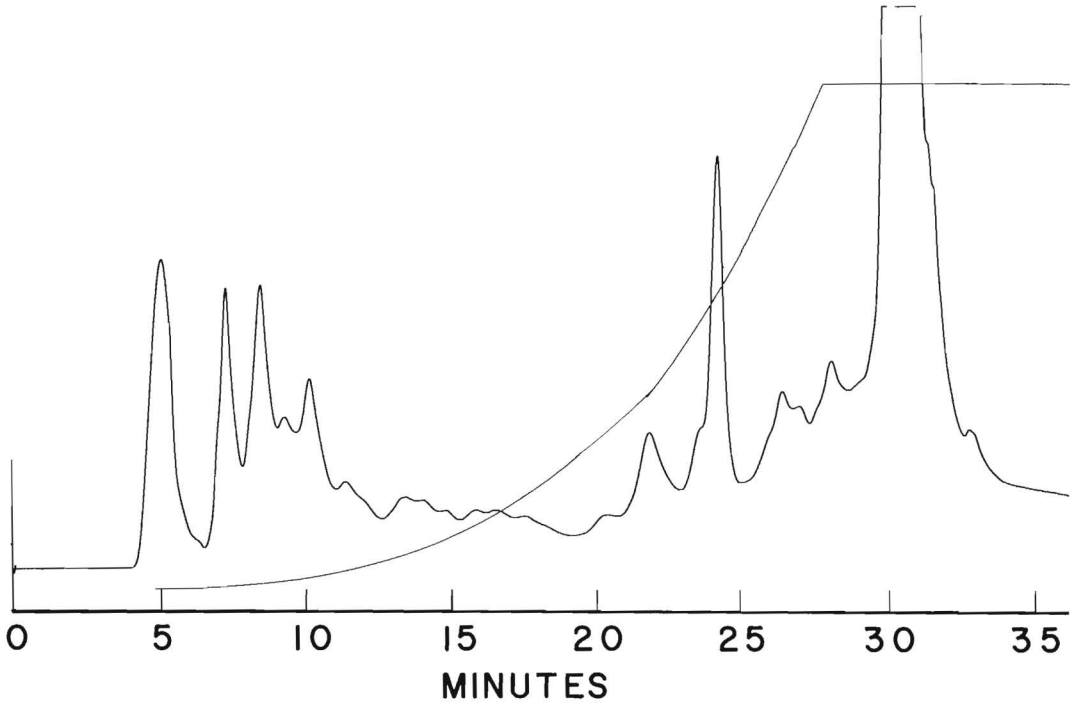

Figure 42. Survey liquid chromatogram of fraction five from vacuum distillation of draft fan wood oil.

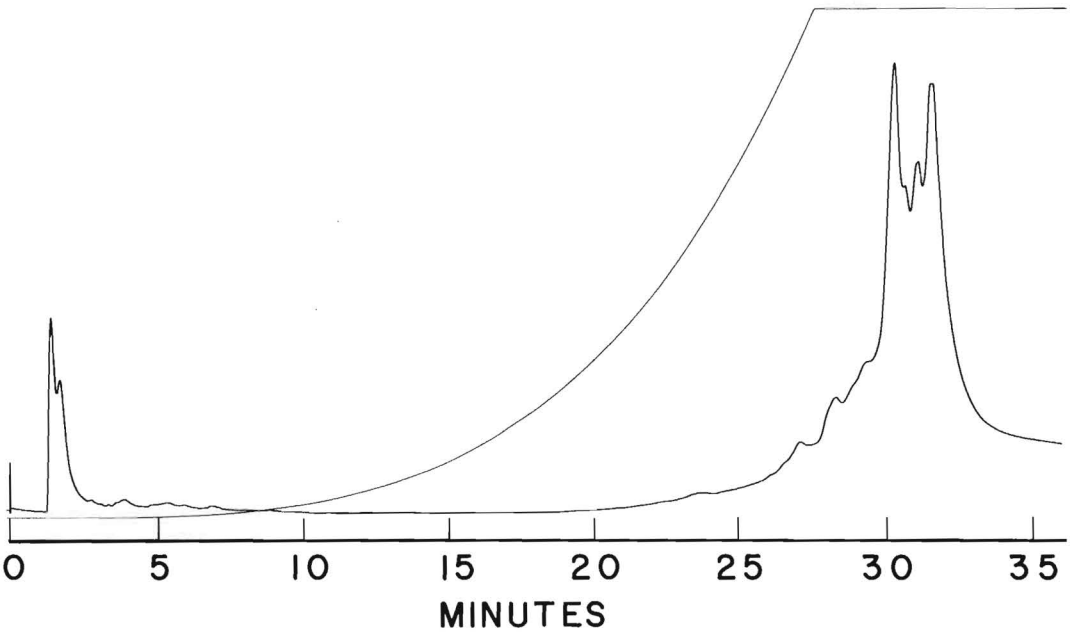

Figure 43. Survey liquid chromatogram of residue from vacuum distillation of draft fan wood oil.

At a head temperature of 105°C, the distillation had slowed down considerably, and the material in the flask was becoming more viscous. The distillation was discontinued at this point. Upon cooling to ambient temperature, the residue in the flask was a very viscous, black tarry material.

Survey liquid chromatograms of fractions 1, 5 and 9 from the spinning band distillation are presented in Figures 44, 45 and 46 respectively. Figure 36 gives a survey liquid chromatogram of the combined oil fractions of the vacuum distilled material used in this distillation.

Steam Distillation

Two separate steam distillations were tried with the condenser oil obtained July, 1976. In the first experiment, 1,238g (14% water) of the condenser oil was used. An oily layer, 8.8 g, along with an aqueous layer of 385 g was collected using steam only at a temperature up to 105°C. At this point heat was applied to the flask in addition to steam injection, and the distillation was continued up to 190°C. The data on the distillates and flask residue are given in Table 13 below. Of the original charge, 18.2% distilled as a separate organic phase, and 11.6% organic material was detected by gas chromatography in the aqueous layers. A recovery of only 78.6% was obtained which indicates that perhaps more organic material was present in the aqueous distillates than was detected. Survey liquid chromatograms of the aqueous phase and of the organic phase obtained (up to 105°C) with steam only are given in Figures 47 and 48, respectively.

TABLE 13. STEAM DISTILLATION DATA - FIRST EXPERIMENT

Material	Temperature		
	Up to 105°C	105°-150°C	150°-190°C
Aqueous Phase	385 g	420 g	279 g
Water	354 g	359 g	228 g
Organic	31 g	61 g	51 g
Organic Phase	8.8 g	33.8 g	183 g
Residue, Organic	--	--	468 g

In the second steam distillation, essentially the same procedure was used except that the flask after the initial steam distillate was collected was only heated to maximum temperature of 160°C. The data from this distillation are given

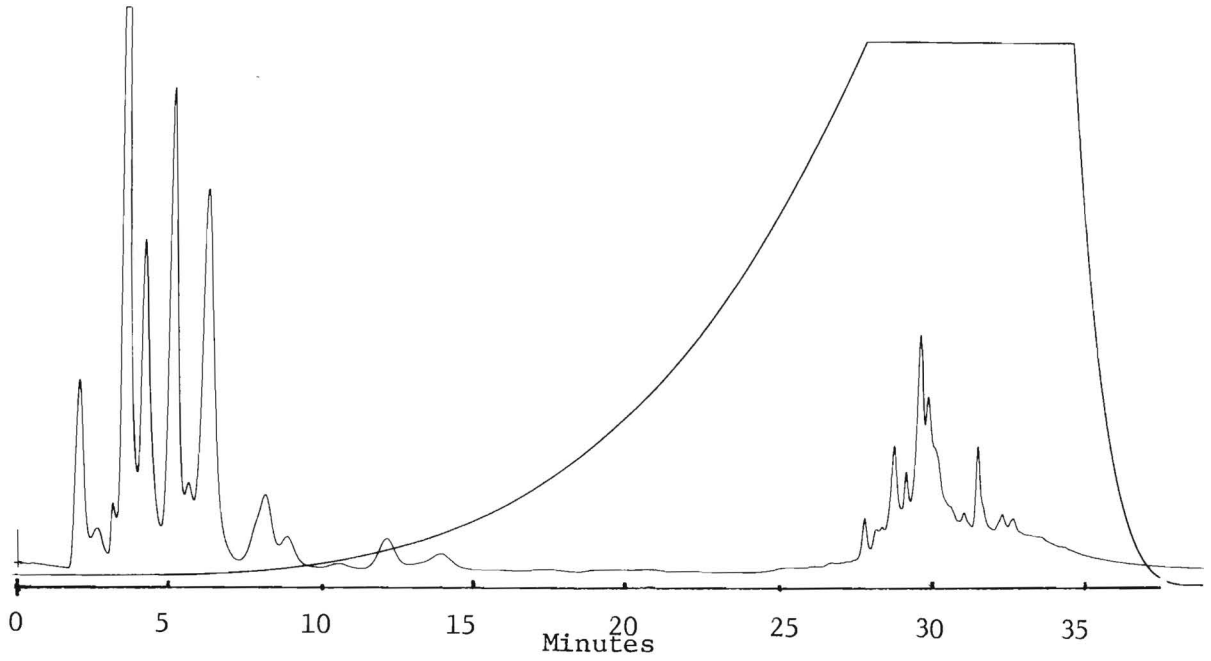

Figure 44. Survey liquid chromatogram of fraction one from vacuum distillation of wood oil with spinning band column.

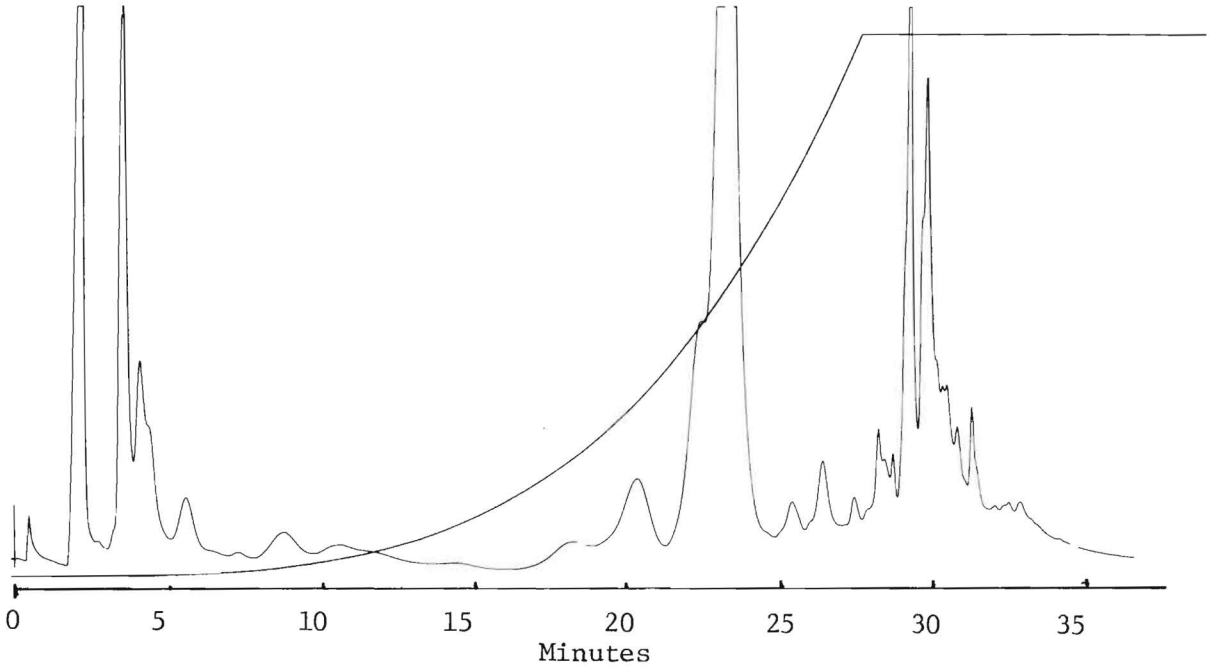

Figure 45. Survey liquid chromatogram of fraction five from vacuum distillation of wood oil with spinning band column.

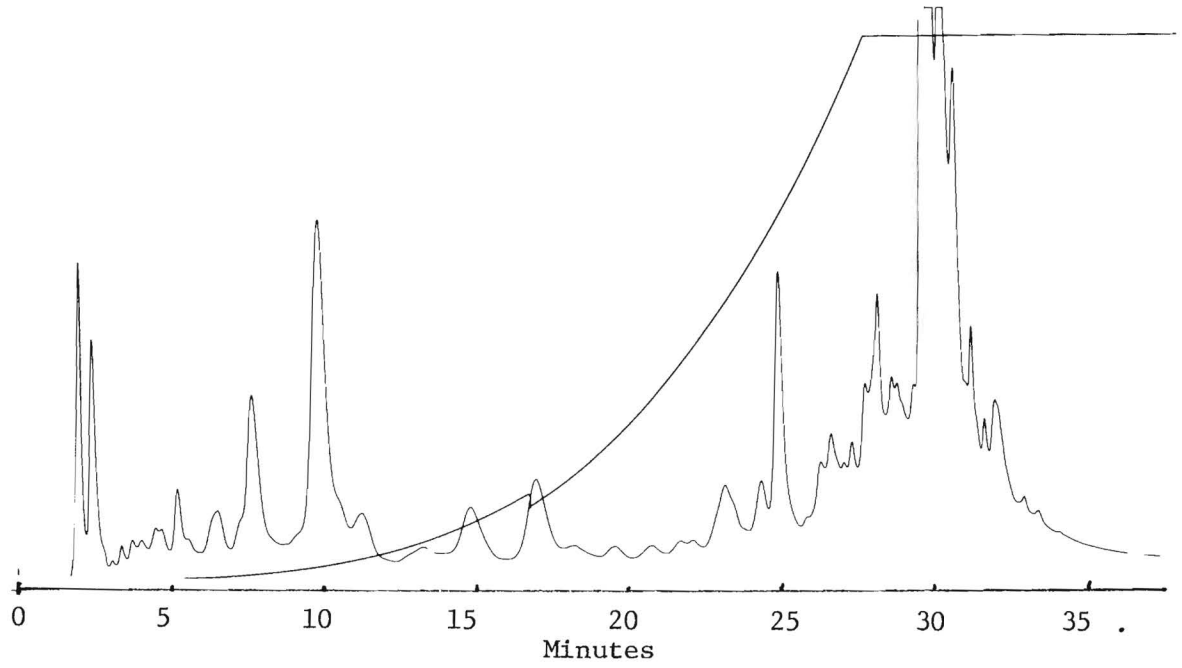

Figure 46. Survey liquid chromatogram of fraction nine from vacuum distillation of wood oil with spinning band column.

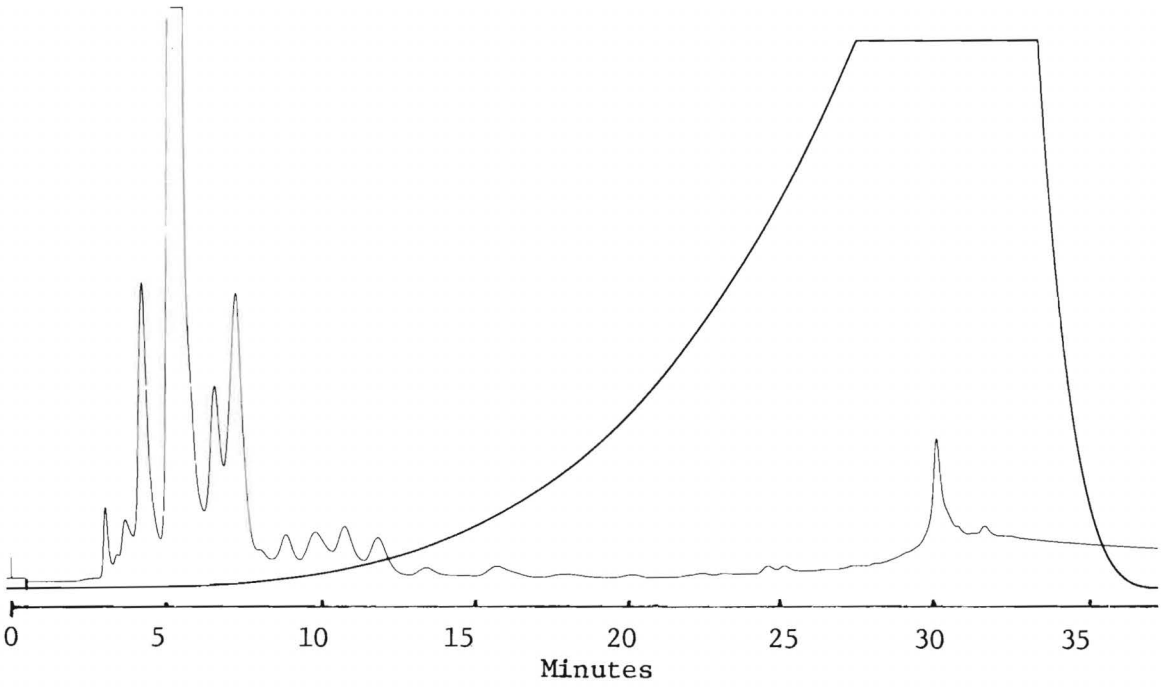

Figure 47. Survey liquid chromatogram of aqueous phase (105°C) from steam distillation of wood oil.

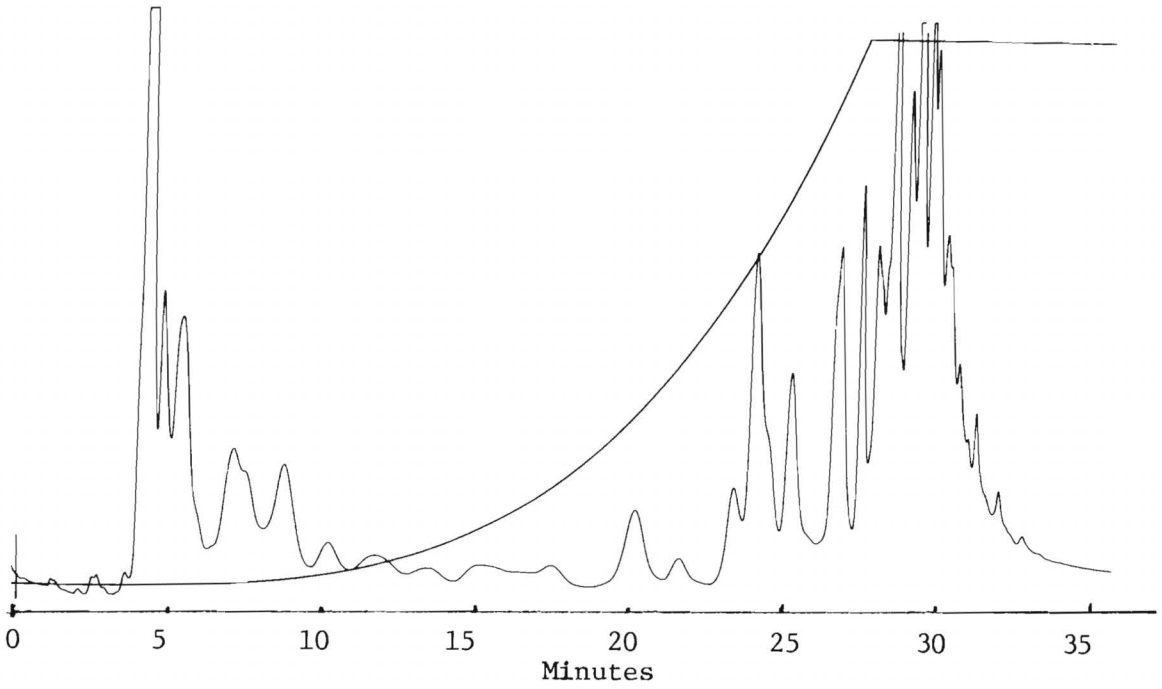

Figure 48. Survey liquid chromatogram of organic phase (105°C) from steam distillation of wood oil.

below. An initial charge of 549 g of condenser oil (14.03% water) was used in this experiment. A total of 414 g of organic material was recovered which represents an 87.6% recovery of the organic material from the raw oil on a dry basis. The data for this distillation is given in Table 14.

TABLE 14. STEAM DISTILLATION DATA SECOND EXPERIMENT

Temperature Range	Up to 108°C	108-160°C
Aqueous Phase	383 g	254 g
Water	365 g	229 g
Organic	18 g	25 g
Organic Phase	7.3 g	14.2 g
Residue	-	361 g
Water		12 g
Organic		349 g

Vacuum Stripping of Water from Wood Oil

The condenser and draft fan wood oils obtained July, 1976, from the 50 dry ton/day facility contained water which does not separate on standing. Samples of the oils without the water were needed for characterization, and vacuum stripping was found to be the most effective means of removing this water. Two experiments for removal of water from condenser oil were carried out at 0.3 mm of mercury. Dry ice-acetone and liquid nitrogen traps were used to recover any water and volatile organics. In the first experiment, the flask was heated to 55°C to insure that the water would be removed. Based on the amount of volatile organics recovered, a second experiment was carried out in which the flask temperature was maintained at 25°C. The data are presented in Table 15 below. A survey liquid chromatogram of the vacuum stripped oil from the second experiment is given in Figure 49.

A sample of draft fan wood oil which has been stored for eight months at 0°C was vacuum stripped for removal of water in the same manner as above for condenser oil in which the flask temperature was maintained at 25°C. The data are presented in Table 16, and a survey liquid chromatogram of the vacuum stripped oil is given in Figure 50.

TABLE 15. VACUUM STRIPPING OF WATER FROM CONDENSER WOOD OIL

Phase	Experiment 1 Heated to 55°C	Experiment 2 25°C
Aqueous Phase		
Water	12.1%	12.9%
Organic	4.4%	0
Organic Phase	0.35%	1.3%
"Dried" Oil	82.4%	84.3%
Total	99.25%	98.5%

TABLE 16. VACUUM STRIPPING OF WATER FROM DRAFT FAN WOOD OIL

Phase	Weight %
Aqueous	15.0%
"Dried" Oil	84.3%
Total	99.3%

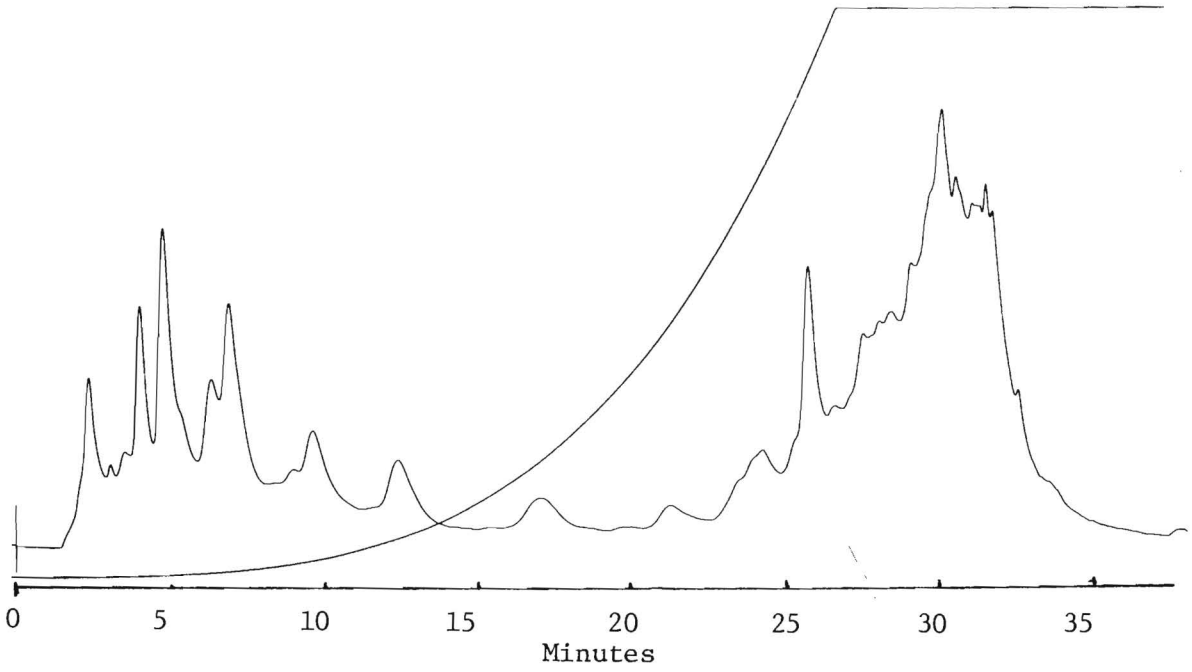

Figure 49. Survey liquid chromatogram of vacuum stripped condenser wood oil.

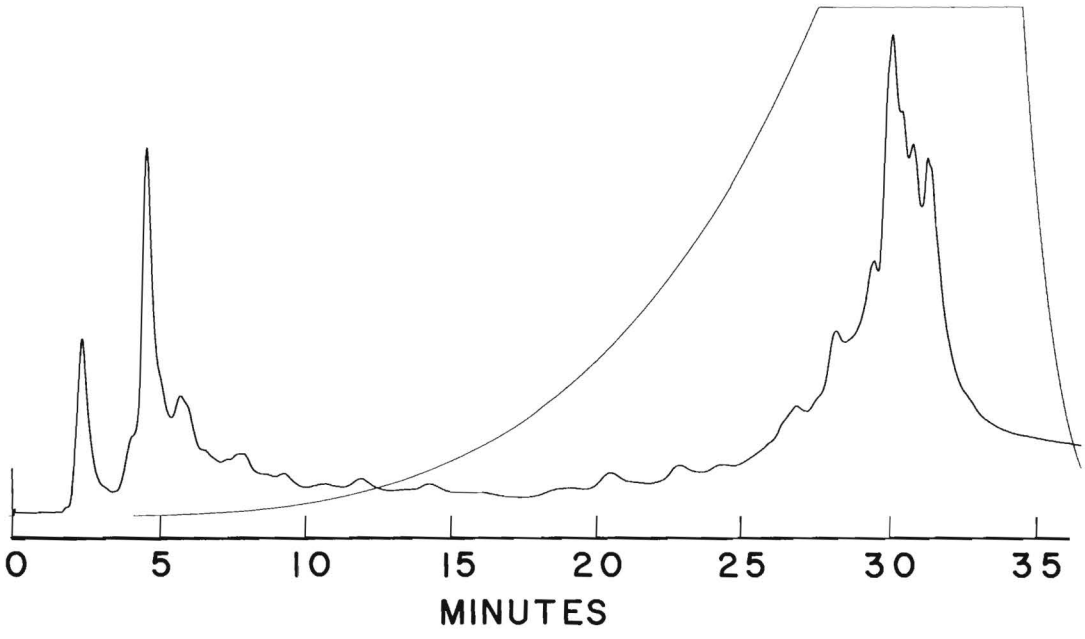

Figure 50. Survey liquid chromatogram of vacuum stripped draft fan wood oil.

SECTION 3

LITERATURE SEARCH

The objective of the literature work is to establish an excellent technical literature base on the pyrolysis of lignocellulosic and carbonaceous materials and of the products formed. This literature base will provide the background for planning experimental programs for maximum resource recovery from lignocellulosic wastes.

The technical literature related to oil obtained by pyrolysis of lignocellulosic materials covers a very broad spectrum. During the first and second quarters the literature was searched for relevant technical papers. Chemical Abstracts were searched from 1948 to the present time and the Industrial Arts Index, which became the Applied Science and Technology Index in 1958, were searched from 1950. The references obtained from this literature search were included as Appendix A in the Quarterly Report No. 2 of this project. The literature work is continuing, and the bibliography will be updated in a later report.

SECTION 4

PUBLICATIONS

A technical paper, "Pyrolysis of Pine Sawdust," was presented at the symposium on Thermal Properties, Pyrolytic Conversion and Combustion of Carbohydrates and Lignins, August 29--September 3, 1976, American Chemical Society, San Francisco. This paper was published as part of the symposium in book form by Academic Press (1976) and is entitled, "Thermal Uses and Properties of Carbohydrates and Lignins," edited by Fred Shafizadeh, Kyosti V. Sarkanan and David A. Tillman. (See Appendix B of quarterly Report No. 2).

A second technical paper, "Wood Oil from Pyrolysis of Pine Bark-Sawdust Mixture," will be presented at the ACS meeting in Chicago, Ill., August 28--September 2, 1977. A preprint of this paper is given in Appendix A.

SECTION 5

RESULTS AND DISCUSSION

The wood oil samples for the initial phases of this study were obtained from the Tech-Air 50 dry ton/day pyrolysis facility located at a lumber yard in Cordele, Georgia. This facility processes a mixture of pine bark and sawdust. Wood oil samples were obtained in July, 1976, and May, 1977. The oil samples have a dark brown color and have a burnt odor. The oils obtained from the off-gas stream generally contains approximately 15% water, which is well emulsified and does not separate on standing. The wood oils are heavier than water, acidic, contain small amounts of solids, have very low ash, exhibit some corrosive properties, have less than 0.01% sulfur and are soluble in polar solvents such as acetone and acetonitrile, but only slightly soluble in hydrocarbon solvents such as hexane and toluene. Samples which were stored for eight months at ambient temperature and $0^{\circ}C$ showed some increase in water content which indicates that reactions are taking place that produce some water. The viscosity increased with two of the samples and decreased with two of the samples. The changes in the measured properties would not have any real effect on the use of the oils as a fuel. Storage of the oil, however, over long periods of time could have effects on the processing of the wood oils into other products. For processing these oils or similar oils, it would be necessary to determine the effect of storage time on process parameters and on quality of products.

Certain properties of the oil were compared with those of numbers 2 and 6 fuel oils. The heating values of the wood oils are lesser than those of the fuels on either a weight or volume basis. Because of the greater density of the wood oils, the heating values of wood oils show a greater percentage value of the heating values of the fuel oils on a volume basis than on a weight basis. The pour points of the wood oils are in the range of pour points of number 6 fuel oil, and the flash points are greater than those of numbers 2 and 6

fuel oils. The viscosity at 25°C for both the condenser and draft fan oils was about the same, about 11 times as great as number 2 fuel oil and about 0.1 that of number 6 fuel oil. The wood oils and similar oils have properties similar to those of petroleum fuel oils and can be utilized as fuels provided the users of the oils are cognizant of these properties.

The wood oils were tested and characterized by a number of procedures which are used for petroleum oils and oils obtained from other sources. Many of these tests are useful as such, but some of them need to be modified to provide more worthwhile information. The ASTMD-36 (Group 3) distillation test was tried several times with a number of wood oil samples. In each case, the wood oils started to decompose when the temperature reached the 260-280°C range at which point approximately 50% of the oil sample had distilled. In several trials, the material boiled over into the condenser. One must exercise extreme care in using this test with wood oils, and since the oils tend to decompose, the data are of doubtful utility.

The viscosity of an oil at different temperatures is of importance in the handling and processing of the oil. Viscosity--temperature curves were determined for the wood oils as received, vacuum stripped, numbers 2 and 6 fuel oils and condenser wood oil samples which had been heated at 110°C for varying time periods. An examination of the viscosity curves in Figures 1 and 2 for the July, 1976, wood oils, and Figure 7 for the May, 1977, wood oils will show that each of these samples as initially received had a different viscosity curve. The viscosity of the samples can be related to the water content. The May, 1977, condenser oil had the least water content (4%) and exhibited the greater viscosity, whereas the May, 1977, draft fan oil had the largest water content (31.4%) and was the least viscous of the samples. Also, it should be noted in Figures 1 and 2 that the viscosity changes with time as determined for the July, 1976, wood oils which had been stored for eight months. The July, 1976, wood oils which had been vacuum stripped for the removal of water had viscosity curves which are very closely related as shown in Figures 3 and 4. A comparison of these curves with the curve for number 6 fuel oil, Figure 6, shows the similarity of these three viscosity curves. Sealed samples of the July, 1976, condenser oil were heated at 110°C for different time periods and the viscosities were determined. The samples were sealed to prevent the loss of volatile material.

An examination of these curves, Figure 5, shows that the viscosity increased significantly with time. The viscosity curve for the sample heated 75 hours is very similar to the viscosity curves for the vacuum stripped wood oils and number 6 fuel oil.

Liquid chromatography is a very versatile and powerful analytical technique for the analysis of complex organic mixtures. It is an excellent technique for the analysis of wood oils obtained by pyrolysis because LC can be carried out at ambient temperature, is useful with a wide variety of solvent systems, is nondestructive and is capable of high resolution of complex mixtures. A considerable amount of effort was spent in developing LC conditions which could be used for both survey and high resolution liquid chromatograms of the raw wood oils and of fractions of oil obtained from them. Our initial objective with LC is to utilize the method to obtain "fingerprints" of the oil samples for comparison and correlation. A representative survey LC of condenser oil is shown in Figure 9 and a representative high resolution LC, Figure 10. LC was used as an analytical technique in all of our distillation work with the wood oils. Efforts will be continued to improve LC analysis of wood oils.

The molecular weight range of the wood oils is of importance in characterizing these oils. In an attempt to obtain some preliminary information about the molecular weight range of the wood oils, the size exclusion LC columns of silica gel with narrow pore size distribution were utilized. The preliminary results indicate that the molecular weight is in the 80-160 range for the wood oils. A sample of still bottoms from a wood oil that was commercially distilled gave a molecular weight range of 112 to 9,000. These results are indicative of the molecular weight range of the raw oils and indicate that higher molecular weight substances are formed when the oils are heated. Additional work is planned to obtain more definitive data on the molecular weight range of the wood oils.

Some preliminary GC analysis of the wood oils and samples from the distillation experiments were carried out. The results from these initial GC analysis show that the raw wood oils contain a large number of components, and that the fractions obtained from the wood oils also contain a relative large number of components. Some representative gas chromatograms are given in

Figures 22 through 33.

Samples of the wood oils were distilled at atmospheric pressure, at low vacuum in a simple distillation apparatus, at low vacuum with a spinning band column, and with steam. In addition, some vacuum stripping experiments were carried out at ~ 0.5 mm mercury for removal of water. In both the atmospheric and simple vacuum distillations, the initial distillate was an aqueous phase which contained some soluble organic components. In the atmospheric distillation, the distillate was mainly the heavy oil with some water and light oil at 125°C to 190°C and at 190°C to 230°C, the distillate was mainly the light oil. An examination of the survey liquid chromatograms of the heavy and light oil distillates in Figures 34 and 35, respectively, showed that each distillate contains a large number of components and indicated that the light oil contains a greater percentage nonpolar components. Approximately 68% of the material distilled before the head temperature started to drop. At this point, it was observed that the material in the flask was showing signs of decomposition and the distillation was stopped. In the simple vacuum distillation of condenser wood oil, approximately 64% of the sample distilled from ambient temperature to 190°C and with draft fan oil, approximately 47% distilled from ambient to 122°C. In these vacuum distillations, the distillations were stopped at those points when the material in the flask showed signs of decomposing.

Survey liquid chromatograms from the simple vacuum distillation of the draft fan oil of the cold trap sample, fractions one through five and the still bottoms are given in Figures 37 through 43 for completeness. An examination of these chromatograms will show that the cold trap material, each distillate fraction, and the still bottoms are complex mixtures and that some separation was achieved. The cold trap sample, which was mostly water, contained a number of components which would represent very volatile components, including both polar and nonpolar components. The chromatograms of fractions one through five showed each fraction contained both polar and nonpolar components, that some components were more concentrated in certain fractions, and that as the distillation temperature increased, the fractions contained relatively more nonpolar components. For example, fraction four, Figure 41, contained a relatively high concentration of intermediate polar components. The chromatogram of the still bottoms, Figure 43, indicated that the still bottoms were very largely nonpolar material.

A sample of the combined oil fractions from the simple vacuum distillation of condenser wood oil was distilled in a spinning band column at 0.2-0.4 mm mercury. Nine fractions were collected over a temperature range of 35° to 105°C and approximately 67% of the material distilled. The head temperature did not show any leveling off during the distillation but showed a gradual rise from 35° to 105°C. At 105°C, the distillation was stopped as the rate of distillation had slowed down considerably and the material in the flask was becoming more viscous. Upon cooling to room temperature, the residue in the flask became very viscous and tarry. Since the starting feed material for this distillation was entirely the distillate from a simple vacuum distillation, the fact that the feed material became viscous and tarry as the distillation progressed is indicative of the heat sensitive nature of the wood oils and fractions obtained from them. An examination of the survey liquid chromatograms of fractions 1, 5 and 9, Figures 44, 45 and 46 respectively, showed that each fraction contained a large number of components, that fraction one contained relatively more polar components than nonpolar, and that as the distillation proceeded with increasing head temperature the amount of nonpolar material increased in the fractions. For example, the chromatogram for fraction 5, Figure 45, showed a large peak at ~ 23 minutes which most likely contained intermediate polar components. The chromatogram of fraction 9, Figure 46, which was the last fraction collected, indicated a much greater amount of nonpolar components in the higher boiling material.

Condenser oil samples were steam distilled in two separate experiments. In the first experiment, 8.8 g of an oily layer and 385 g of an aqueous phase were collected using steam. Then application of heat along with steam injection up to 190°C produced additional aqueous and oily phases. The data for the first distillation is given in Table 13. In the second steam distillation, 7.3 g of an oily layer was obtained with 383 g of an aqueous layer. The application of heat along with steam injection up to 160°C produced an additional aqueous phase and an oily phase. The data for this distillation is given in Table 14. A very small percentage (~1%) of the wood oils distilled with use of steam alone. The aqueous layers contain from 4.7 to 8% dissolved organic components as determined by GC. Additional distillate can be obtained

by application of heat to raise the temperature. Survey chromatograms of the aqueous phase and of the oily phase obtained by steam alone from the first experiment are given in Figures 47 and 48. The aqueous phase contains also all polar compounds whereas the oily phase contains a much greater percentage of the intermediate polar and nonpolar material.

In order to obtain samples of the wood oils without water, it was found that removal of the water could be accomplished at reduced pressure, less than 1 mm mercury pressure, without heat. For example the 12.9% of water removed from the condenser wood oil in experiment 2, Table 15, compared favorably with the 14% water as determined by the Dean-Stark method. In the case of the draft fan wood oil sample which had been stored for 8 months at 0°C, the 15.0% water removed under vacuum compares very favorably with the 15.5% as determined by the Dean-Stark method. Survey liquid chromatograms of the condenser oil and draft fan oil are given in Figures 49 and 50 respectively.

SECTION 6

SUMMARY

Samples of wood oils were obtained from the Tech-Air 50 dry ton/day pyrolysis facility which processes a mixture of pine bark and sawdust in July, 1976, and May, 1977. These samples were characterized and tested by a number of standard analytical and test procedures. Many of the analytical and test procedures are applicable for use with oils obtained by pyrolysis of lignocellulosic materials such as agricultural, forestry and municipal wastes. However, modifications of some of the procedures are needed to provide meaningful results. In addition, some new analytical tests may be needed for certain applications so as to provide necessary data for evaluation of the oils. The wood oils from the Tech-Air facility were dark brown with a burnt odor and contained water in the range of 5 to 15% which was well emulsified and does not separate on standing. The wood oils were acidic, had very low ash, exhibit slight corrosive properties and contained less than 0.01% sulfur. The oils were soluble in polar solvents such as acetone and acetonitrile, but were only slightly soluble in nonpolar solvents such as hexane and toluene. Oil samples stored for eight months showed no major significant change in the properties checked that would have any real effect on the use of the oils as a fuel. The viscosity temperature curves for a number of the oils were determined. The amount of water in the oil has a decided effect on the viscosity. As the water content decreases the viscosity increases. For example, the wood oils which were vacuum stripped for the removal of water had viscosity curves which were very similar to the viscosity curve for number 6 fuel oil. The viscosity of the wood oils increased when heated in sealed containers for extended periods of time at constant temperature. It would be necessary to take into account the effect of heat in the utilization and processing of the oils.

Liquid chromatography (LC) was found to be very useful as an analytical technique for the analysis of the oils and fractions obtained from them. LC is is being used to follow our distillation experiments and will be used in future

work in processing the oils. Preliminary results with size exclusion LC columns indicate that the molecular weight range for the wood oils is 80 to 160. Additional work is planned to obtain more definitive data on the molecular weight range of the wood oils.

Gas chromatography (GC) is a powerful technique for the analysis of complex organic mixtures and was used in the analysis of some fractions obtained in the distillation experiments. The heat sensitivity of the wood oils must be taken into account in using GC in the analysis of these materials. Additional effort will be expended in developing proper GC procedures for use with the wood oils.

A number of distillation experiments were carried out with the wood oils to obtain information on distillation as a processing method. The distillation experiments included atmospheric distillations, simple vacuum distillation, fractionation under vaccum with spinning band column and steam distillation. In the atmospheric and vacuum distillations, after about 70% of the oil had distilled, the material in the flask had became more viscous and began to show signs of decomposition. The fractions obtained from these distillations contained a large number of components as shown by LC. The LC chromatograms from the vacuum distillations showed that some separation can be achieved and indicated that the lower boiling fractions contained more polar components, the higher boiling fractions contained components of more nonpolar nature, and the still bottoms contained mostly nonpolar material. Steam distillation of the wood oils produced very small amounts of organic distillates with only steam injection. Larger quantities of organic distillate could be obtained by application of heat to the distilling flask. Additional work with steam distillation would be needed in order to determine if some very useful products could be obtained from the wood oils by this process.

The wood oils are complex organic mixtures and contain components which vary in chemical nature from the very polar to nonpolar. The wood oils are heat sensitive, and this characteristic must be considered in the handling and processing of the oils. Distillation offers a processing method for separation of the oils into fractions of different boiling ranges. The low boiling fractions contain more polar components and the higher boiling fractions, more nonpolar components.

SECTION 7

PLANS FOR FUTURE WORK

The work program for the next reporting period will include the following areas. Pyrolysis experiments of waste forestry materials will be carried out in two different experimental modes in a six inch tube furnace with a condensation train for recovery of condensible products (1). The results of these experiments will yield data and information on the effect of different experimental pyrolysis modes on the yields and quality of products. The condensible oils are of particular interest.

The characterization and testing work of the oils will be continued. Emphasis will be placed on those properties which will yield meaningful and significant information in the testing of oils produced by thermal decomposition of lignocellulosic materials.

Preliminary extractive and separation work will be initiated with the oils. The objective of this phase of the program is to develop procedures for separating the oils into groups or classes of compounds, such as acidic, phenolic, and aromatic components. By separation of the oils into groups of similar chemical species, it should be possible to develop specific uses for these fractions.

Characterization efforts to determine the chemical species in the oils and fractions obtained from the oils will be continued. Liquid chromatography gas chromatography and infrared will be used in this phase of the work.

The literature search for current relevant technical articles will be continued.

REFERENCES

1. Knight, J. A. Pyrolysis of Pine Sawdust. In: Thermal Uses and Properties of Carbohydrates and Lignins, edited by F. Shafizadeh, K. V. Sarkanan and D. A. Tillman. Academic Press, 1976. pp. 159-173.

2. Knight, J. A., M. D. Bowen and K. R. Purdy. Pyrolysis - A Method for Conversion of Forestry Wastes to Useful Fuels. Presented at Conference on Energy and Wood Products Industry, Forest Products Research Society, Atlanta, Georgia, November 15-17, 1976.

APPENDICES

APPENDIX A

Publication

"Wood Oil from Pyrolysis of Pine Bark-Sawdust Mixture"

J. A. Knight
D. R. Hurst
L. W. Elston

To be presented at

American Chemical Society
Chicago, Ill.

August 28-September 2, 1977

APPENDIX B

EXPENDITURES

June 21, 1976-May 31, 1977

APPENDIX A

WOOD OIL FROM PYROLYSIS OF PINE BARK-SAWDUST MIXTURE*

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I. INTRODUCTION

Pyrolysis has received considerable attention in the last several years as a method for converting waste materials--agricultural, silvicultural, and municipal refuse--into useful products, particularly fuels, and at the same time, serving as a satisfactory disposal method. Pyrolysis is now receiving consideration as a process for the conversion of biomass from biomass plantations into useful products, particularly fuels [1]. Pyrolysis of lignocellulosic materials produces a char, condensible organic substances, water and noncondensible gases. The char and condensible organic liquid can be utilized as clean burning fuels, and the noncondensed gas is a low Btu fuel that must be used on site.

Workers at the Engineering Experiment Station (EES) have found that pyrolysis is readily adaptable for the conversion of a variety of cellulosic and lignocellulosic materials into useful fuels and other products. During the past eight years, a steady-flow, low temperature pyrolysis system has been developed which involves processing of the feed material in a continuous operation in a porous, vertical bed [2]. The Tech-Air Corporation,+ licensee for the process, has successfully operated a 50 dry ton/day field demonstration pyrolysis facility at a lumber yard at Cordele, Georgia. The feed material utilized at this facility is a mixture of pine bark and sawdust.

* Supported in part by E.P.A. Grant No. R804 416 010.
+ Tech-Air Corporation, Atlanta, Georgia

The physical and chemical characteristics of the oils obtained from the pyrolysis of various types of waste materials are needed for the proper evaluation and utilization of these oils. These data are also useful in establishing the pyrolysis operating conditions for production of the most suitable oils. There are many available testing and characterization procedures that have been developed for petroleum, vegetable and other oils, and some of these or modifications will prove useful for oils obtianed by pyrolysis of lignocellulosic wastes. The data presented below were obtained on wood oils produced in the Tech-Air field demonstration pyrolysis facility.

II. WOOD OIL SAMPLES

Approximately 110 gallons of oil for this study were collected on July 15, 1976, at the Tech-Air field demonstration facility while the unit was operating in a steady state mode. Approximately equal quantities of oil were obtained from the air cooled condenser and the draft fan, which is located between the condenser and the after-burner for the noncondensed gases. Samples of both oils were stored at ambient temperature and $0^{o}C$ for future characterization and use. A representative sample of the feed material, a mixture of pine bark-sawdust, had the characteristics and properties as listed in Table I, and the results of the characterization and analyses of representative samples of both oils are given in Table II.

TABLE I.

Properties of Pine Bark-Sawdust Feed Material

Property	Result	Method
Pinebark / Pine sawdust	70 / 30	Microseparation by visual means
Bulk density	21.3 kg/cu m 13.3 lbs/cu ft	
Moisture	10.3%	ASTM D-1762-64
Ash (weight %)	1.3%	ASTM D-1762-64
Acid Insoluble Ash (weight %)	<0.1%	
Heating Value (dry basis)	5061 cal/g 9109 Btu/lb	ASTM D-240-74

TABLE II.

Properties of Wood Oils from Tech-Air 50 Dry Ton/Day Facility

Property	Condenser Oil	Draft Fan Oil	Method
Density	1.1415 g/ml 9.525 lbs/gal	1.1075 g/ml 9.242 lbs/gal	-
Water content (weight %)	14.0%	10.4%	ASTM D 95-70
Heating Value (wet basis)	5,056 cal/g 9,100 Btu/lb	5,883 cal/g 10,590 Btu/lb	ASTM D 240-64
pH	2.9	3.3	5% Oil dispersed in water
Acid Number	75 mg KOH/g	31 mg KOH/g	ASTM D-664-58
Flash Point	111°C 233°F	121°C 240°F	ASTM D-93-73
Filterable Solids (weight %)	0.3%	0.4%	Acetone Insoluble
Copper Strip Corrosion	1	1	Classification-ASTM D-130-7
Sulfur (weight %)	<0.01%	<0.01%	ASTM D-129-64
Pour Point	26.7°C 80°F	26.7°C 80°F	ASTM D-97-66
Ash (weight %)	0.08%	0.03%	-
Distillation			ASTM D-86
First Drop	98°C	101°C	Group 3
10% Point	103°C	105°C	
48% Endpoint	NA	265°C	
53% Endpoint	282°C	NA	
Solubility (weight %)			
Acetone	99.6%	99.6%	
Methylene Chloride	93.5%	97.8%	
Toluene	Slightly	Slightly	
Hexane	Slightly	Slightly	
Elemental Analysis (weight %)			
Carbon	51.2	65.6	
Hydrogen	7.6	7.8	
Nitrogen	0.8	0.9	

Certain properties were redetermined on samples of the oil, which had been stored at $0^{o}C$ and ambient temperatures for approximately eight months, and these results along with the initial values are given in Table III.

TABLE III.

Variation of Oil Properties Over Eight Months Period

Property	Condenser Oil		
	Initial Value	Stored Eight Months	
		$0^{o}C$	Ambient Temperature
Water Content (weight %)	14.0%	20.5%	24.1%
Heating Value (wet basis)	5,056 cal/g 9,100 Btu/lb	5,444 cal/g 9,800 Btu/lb	5,106 cal/g 9,190 Btu/lb
Acid Number	75 mg KOH/g	87 mg KOH/g	89 mg KOH/g
Viscosity[1]	275 cP	350 cP	175 cP
pH	2.6	3.4	2.9

Property	Draft Fan Oil		
	Initial Value	Stored Eight Months	
		$0^{o}C$	Ambient Temperature
Water Content (weight)	10.4%	15.5%	12.7%
Heating Value (wet basis)	5,883 cal/g 10,590 Btu/lb	5,922 cal/g 10,660 Btu/lb	5,939 cal/g 10,690 Btu/lb
Acid Number	31 mg KOH/g	71 mg KOH/g	60 mg KOH/g
Viscosity[1]	233 cP	79 cP	475 cP
pH	3.3	3.1	3.0

[1] Determined with Brookfield Viscosimeter, Model LV with Thermosel system at $25^{o}C$ at 60r/min.

One significant use of these and similar oils is as a fuel. Therefore, it is of interest to compare some typical properties of the condenser and draft fan wood oils with Number 2 and 6 fuel oils. These values are given in Table IV below. It is of interest to note that because of the greater densities of the wood oils, the heating values of the wood oils when compared on a volume basis

are larger percentages of the heating values of the fuels oils than when compared on a weight basis. The very low sulfur content of the wood oils is a significant property for the utilization of these wood oils as fuels. Proper blending of wood oils with high sulfur fuels oils can serve as a means of reducing the overall sulfur content of the combined fuel, and consequently, sulfur emissions.

TABLE IV.

Typical Properties of Wood Oils and Fuel Oils

Property	Wood Oils[1]		Fuel Oils[2]	
	Condenser	Draft Fan	#2	#6
Water Content, %	14	10.4	Trace	2
Btu/lb	9,100	10,590	19,630	18,590
Btu/gal	86,700	97,850	139,400	148,900
Density, g/ml	1.142	1.108	0.851	0.960
lb/gal	9.53	9.25	7.10	8.01
Pour Point	80°F	80°F	0°max	65-85°F
Flash Point	233°F	240°F	100°F min	150°F
Viscosity, cP[3]	225	233	20	2262
Elemental Analysis				
Carbon %	51.2	65.6	86.1	87.0
Hydrogen %	7.6	7.8	13.2	11.7
Nitrogen %	0.8	0.9	-	-
Sulfur %	<0.01	<0.01	0.6-0.8	0.9-2.3

1. Values obtained on oils with moisture content as reported.
2. Values for fuel oils are considered typical. Sulfur will vary depending origin of oil. Ref., North American Combustion Handbook, 1st ed., North American Mfg. Com., Cleveland, Ohio, 1952.
3. Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25°C at 60r/min.

III. VISCOSITY

The viscosity of liquids and its change with temperature is a significant property, particulary with liquids that will be handled by pumping. The viscosity values for the wood oils in this study were determined with a Brookfield viscosimeter, Model LV, with Thermosel system. The vicosity versus temperature was determined for both the condenser and draft fan oils initially and on samples

which had been stored at $0^{\circ}C$ and ambient temperature for approximately eight months. These viscosity curves are given in Figures 1 and 2. The viscosity versus temperatures curves of samples of both oils which had been vacuum stripped for removal of water, as described in Section IV E, are given in Figures 3 and 4. In order to determine the effect of prolonged heat upon the viscosity of condenser oil, samples of sealed oil were heated at $110^{\circ}C$ for different time periods, and the viscosity was then determined for each sample. These data are presented in Figure 5. For comparison, the viscosities of the condenser oil and Numbers 2 and 6 fuel oils are presented in Figure 6.

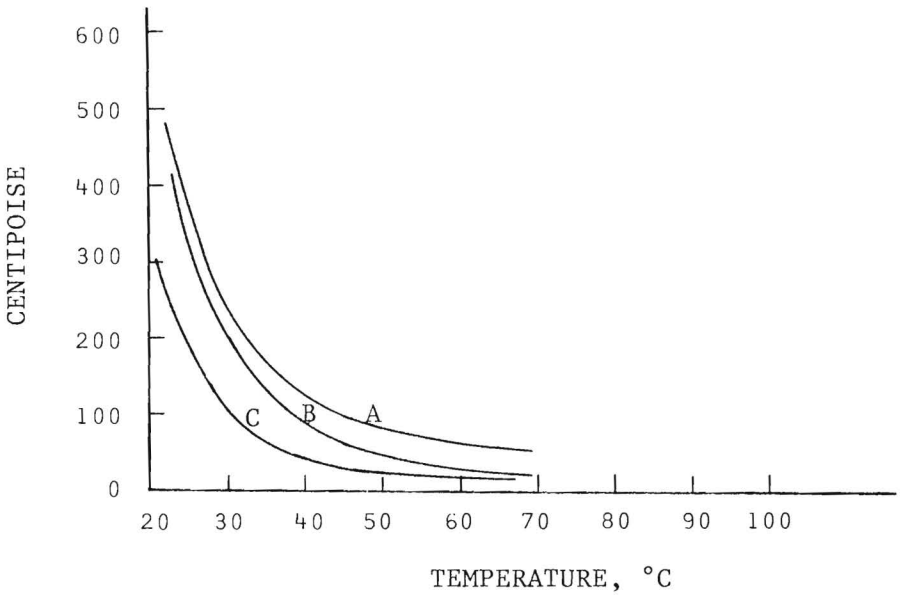

Figure 1. Viscosity of condenser oil

A - Initial viscosity curve

B - Sample stored at 0° C for eight months

C - Sample stored at ambient temperature for eight months

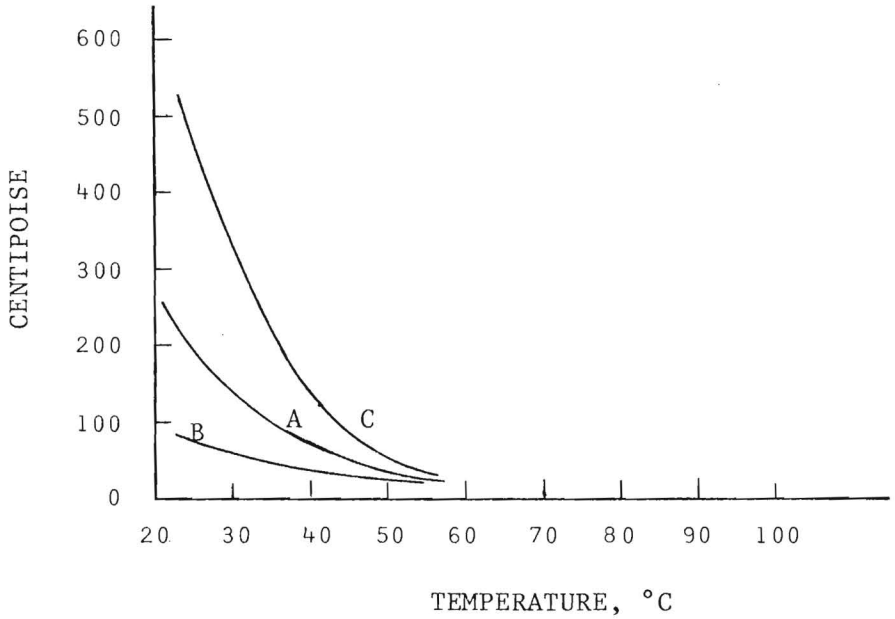

Figure 2. Viscosity of draft fan oil

A - Initial viscosity curve

B - Sample stored at 0° C for eight months

C - Sample stored at ambient temperature for eight months

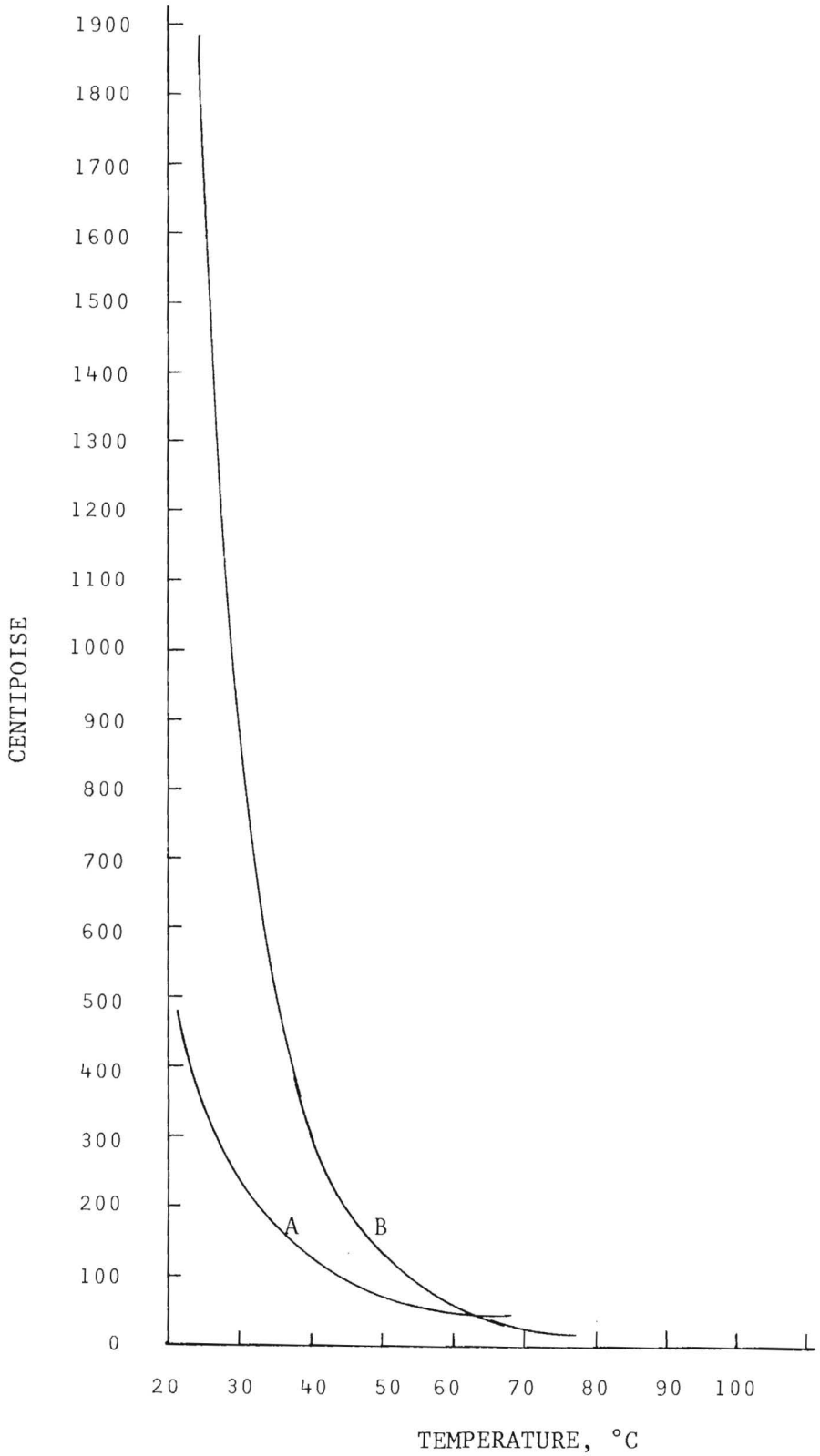

Figure 3. Vacuum stripped condenser oil

A - Initial viscosity curve

B - Vacuum stripped viscosity curve

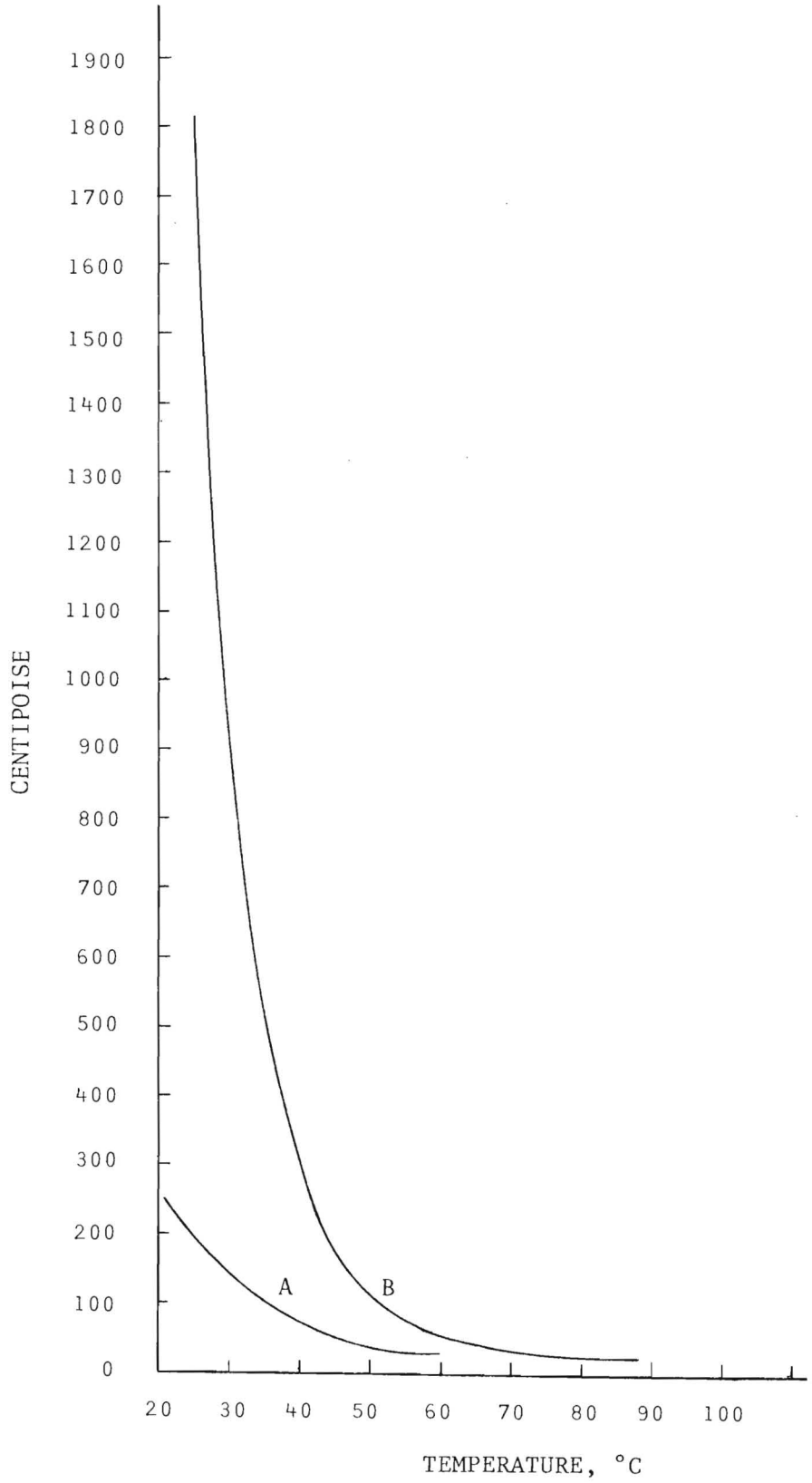

Figure 4. Vacuum stripped draft fan oil

A - Initial viscosity curve

B - Vacuum stripped viscosity curve

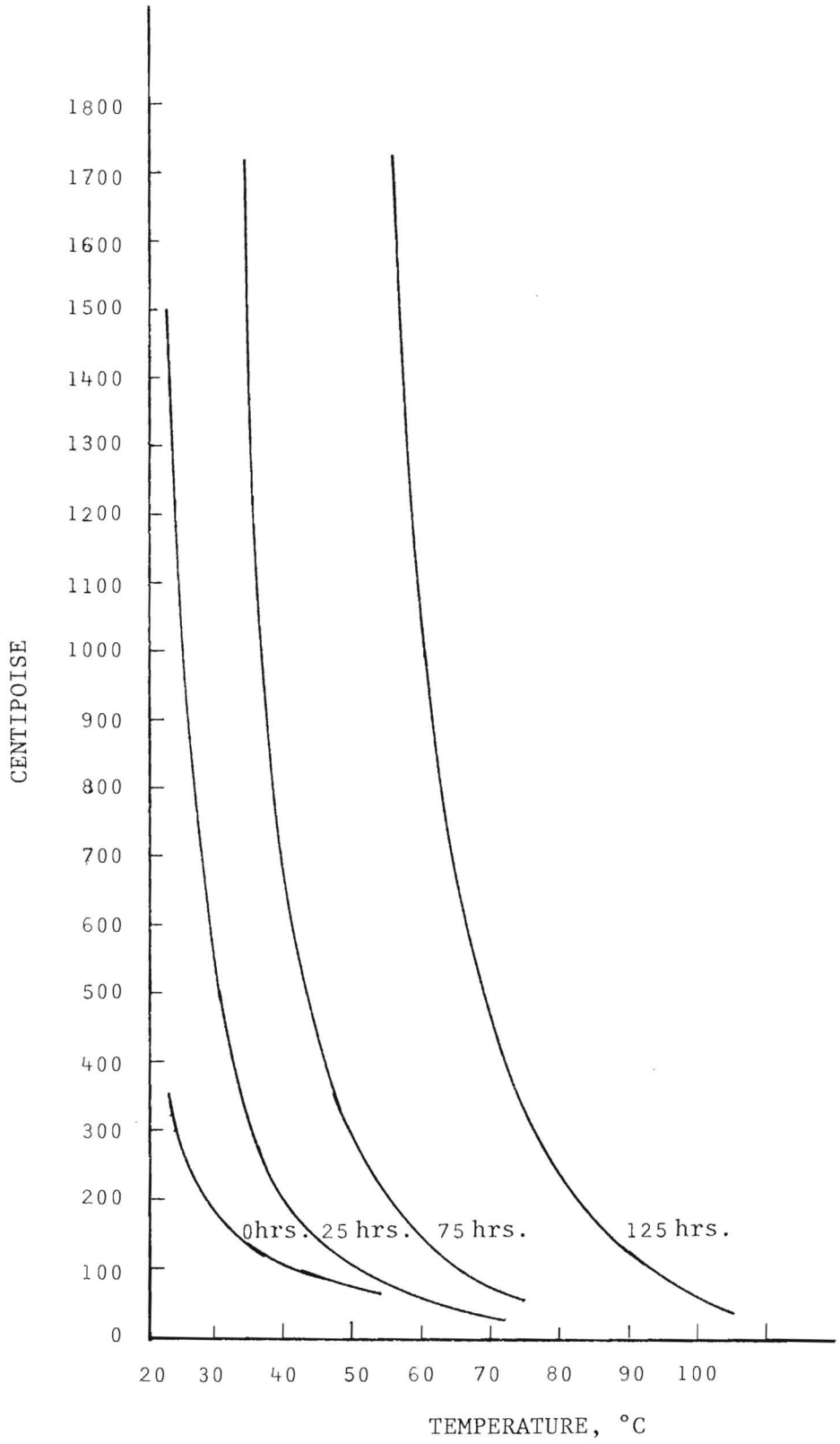

Figure 5. Effect of heating condenser oil at 110°C for different time periods on viscosity

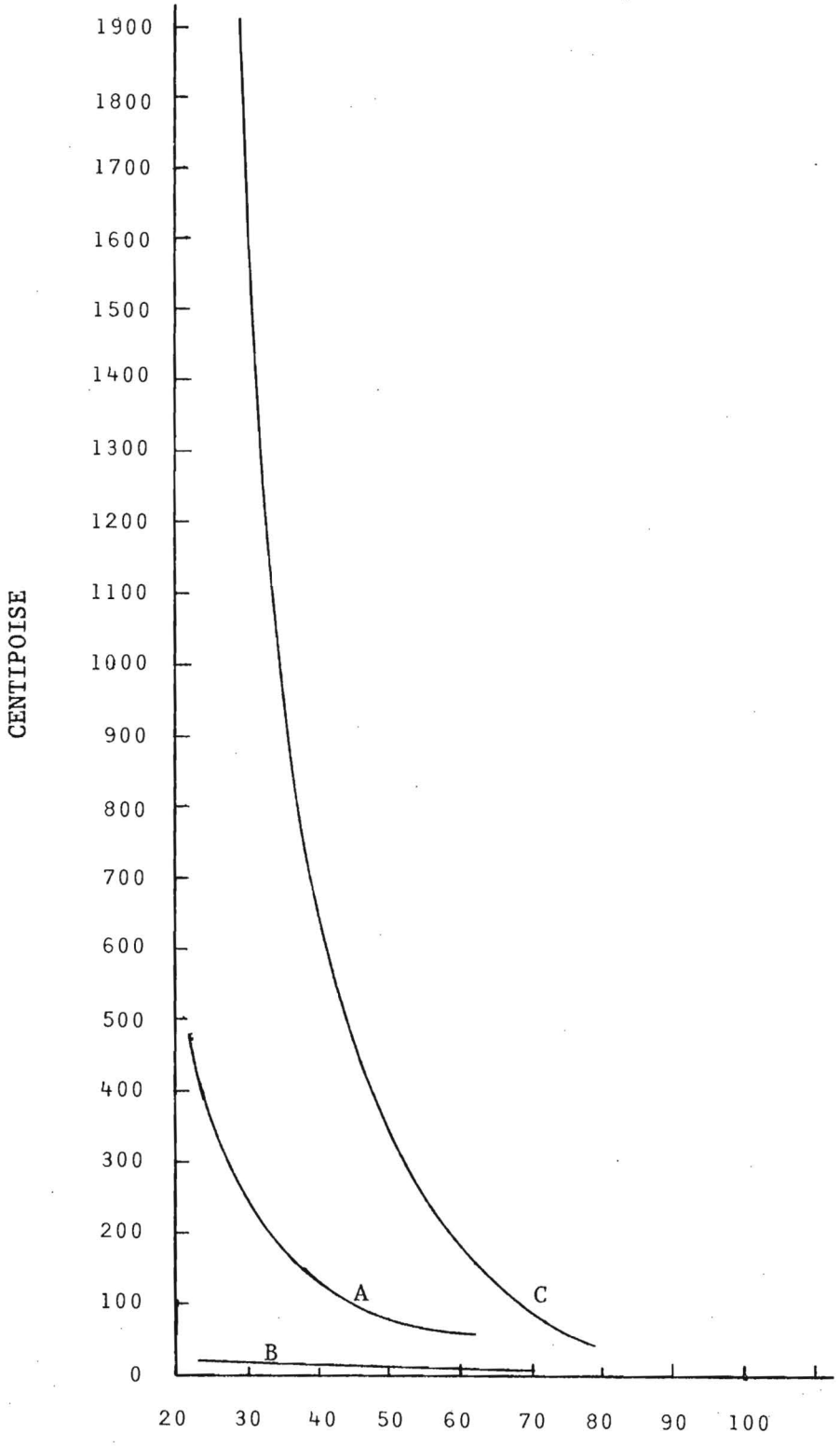

Figure 6. Viscosity curves for condenser oil (initial) and No. 2 and No. 6 fuel oils

A - Condenser oil

B - No. 2 Fuel oil

C - No. 6 Fuel oil

IV. DISTILLATION

Distillation offers a possible method for processing wood oil and similar produced oils to produce more desirable and useful products. Therefore, samples of the condenser wood oil were distilled under a variety of conditions as part of this study.

A. Distillation at Atmospheric Pressure

A sample of condenser oil was distilled at atmospheric pressure, and three distillate phases were obtained--an aqueous phase, a heavy oil phase and a light oil phase. Most of the aqueous phase was obtained at 95°-125°C. Between 125°-190°C, the distillate was mostly heavy oil with some water and light oil. Between 190°-230°C, the distillate was mainly light oil. After approximately 68% of the sample had been collected as distillates, the head temperature began to drop, and the distillation was discontinued. The distillation data are presented in Table V.

TABLE V

Atmospheric Distillation Data

Fraction	Head Temperature, °C	Yield, %
Aqueous Phase[1]	95°-125°	20.7
Heavy Oil	105°-190°	28.4
Light Oil	190°-230°	19.1
Residue[2]		25.0
		93.2

1. Contained 6.2% organic material as determined by gas chromatography.
2. The residue solidified on cooling to room temperature.

The analytical data on the oil phases and the residue are presented in Table VI.

TABLE VI

Analytical Data--Atmospheric Distillation Fractions

Property	Light Oil	Heavy Oil	Residue
Density, g/ml	0.9988	1.0423	--
pH	3.5	2.9	--
Acid No., mg KOH/g	52	17.8	--
Elemental Analysis			
Carbon %	67.4	74.0	60.1
Hydrogen %	7.5	8.2	2.9
Nitrogen %	0.1	0.7	0.8

B. Vacuum Distillation

A sample of condenser oil was distilled in a simple vacuum distillation apparatus at 0.2-0.4 mm Hg pressure with dry-ice and liquid nitrogen traps for recovery of volatile material. The aqueous phase containing light organics was obtained before the head temperature reached 43°C. At 190°C head temperature, the distillation was discontinued as the material in the flask was becoming more viscous and appeared to be approaching a decomposition stage. The vacuum distillation data are presented in Table VII.

TABLE VII

Vacuum Distillation Data

Fraction	Head Temperature, °C	Yield,%
Aqueous and light organics phase[1]	Ambient to 43°	23.1
1	43°-125°	17.6
2	125°-140°	2.1
3	140°-180°	18.5
4	180°-190°	2.6
Residue	--	32.4
		96.3

1. Contained 46% organic material as determined by gas chromatography.

The oil fractions one through four were combined to obtain a sample of oil for fractionation under vacuum with a spinning band column. Analytical data on the combined oil fractions is given in Table VIII.

TABLE VIII

Analytical Data--Vacuum Distillation

Property	Combined Fractions 1-4
Density, g/ml	1.091
pH	2.8
Acid No., mg KOH/g	59.6
Heating value, cal/g	
Btu/lb	10,964
Elemental Analysis	
Carbon, %	62.7
Hydrogen, %	7.7
Nitrogen, %	0.3

C. Vacuum Spinning Band Distillation

A sample of the combined oil fractions from the vacuum distillation (B above) was distilled in a Nester-Faust spinning band distillation column at 0.2-0.4 mm pressure with liquid nitrogen traps for recovery of volatile material. The distillation data are given in Table IX below.

TABLE IX

Spinning Band Distillation Data

Fraction	Head Temperature, °C	Yield, %
1	35-48	8.0
2	48-58	14.6
3	58-60	8.5
4	60-68	2.1
5	68-74	6.9
6	74-82	6.0
7	82-88	4.6
8	88-98	2.8
9	98-105	5.5
Flask Residue	--	30.0
Trap Material	--	7.8
		96.8

At a head temperature of 105°C, the distillation had slowed down considerably, and the material in the flask was becoming more viscous. The distillation was discontinued. Upon cooling to ambient temperature, the residue in the flask was a very viscous, black tarry material. Additional data on some of the fractions are presented in Section V.

D. Steam Distillation

A sample of condenser oil, 1,238 g (14.0% water), was steam distilled. An

oily layer, 8.8 g, along with an aqueous layer of 385 g was collected using steam only at a temperature up to 105°C. At this point heat was applied to the flask in addition to steam injection, and the distillation was continued up to 190°C. The data on the distillates and flask residue are given in Table X below.

TABLE X

Steam Distillation Data

Material	Temperature		
	Up to 105°C	105°-150°C	150°-190°C
Aqueous Phase	385 g	420 g	279 g
Water	354 g	359 g	228 g
Organic	31 g	61 g	51 g
Organic Phase	8.8 g	33.8 g	183 g
Residue, Organic	--	--	468 g

Of the original charge, 18.2% distilled as a separate organic phase, and 11.6% organic material was detected by gas chromatography in the aqueous layers. A recovery of only 78.6% was obtained which indicates that perhaps more organic material was present in the aqueous distillates than was detected.

E. Vacuum Stripping of Water from Wood Oil

The condenser and draft fan wood oils obtained from the 50 dry ton/day facility contained water which does not separate on standing. Samples of the oils without the water were needed for characterization, and vacuum stripping was found to be the most effective means of removing this water. Two experiments for removal of the water were carried out at 0.3 mm of mercury. Dry ice-acetone and liquid nitrogen traps were used to recover any water and volatile organics. In the first experiment, the flask was heated to 55°C to insure that the water would be removed. Based on the amount of volatile

organics recovered, a second experiment was carried out in which the flask temperature was maintained at 25°C. The data are presented in Table XI below.

TABLE XI

Vacuum Stripping of Water from Condenser Wood Oil

	Weight	
	Experiment 1	Experiment 2
Phase	Heated to 55°C	25°C
Aqueous Phase		
Water	12.1	12.9
Organic	4.4	0
Organic Phase	0.35	1.3
"Dried" Oil	82.4	84.3
Total	99.25	98.5

V. LIQUID CHROMATOGRAPHY

Liquid chromatography (L.G.) was selected as one analytical technique that could be used for characterization of wood oils and fractions obtained from them. L.G. appeared to be particularly suitable for these oils since L.G. is carried out at ambient temperture, is capable of high resolution of complex mixtures, and detection of components is nondestructive. The main initial objective of utilizing L.C. in our work with wood oils obtained by pyrolysis is to use a method for "fingerprinting" the raw oils and fractions obtained from them for comparsion and correlation. From preliminary experimental work, the conditions for obtaining survey L.C. chromatogtams are as follows: Partisil ODS 5μ column; water-acetonitrile solvent system with 10 to 100% acetonitrile solvent gradient; and the uv detector set at 254 nm.

Representative chromatograms of raw condenser and draft fan oils are given in Figures 7 and 8, respectively; of the distillate from simple vacuum distillation of condenser oil, Figure 9; of fractions 1, 5 and 9 from the vacuum distillation of the oil distillate from the simple distillation of condenser oil, Figures 10, 11 and 12, respectively; of vacuum stripped condenser oil, Figure 13; and of organic and aqueous phases from steam distillation of condenser oil, Figures 14 and 15.

VI. RESULTS AND DISCUSSION

The wood oils for this study were obtained from the 50 dry ton/day demonstration facility of the Tech-Air Corporation. The feed material was a mixture of pine bark-sawdust in a ratio of approximately 70:30. The pyrolytic converter is a vertical shaft type reactor in which the feed material is fed in at the top giving a vertical, porous bed of the feed material. Char is removed at the bottom and the gaseous phase passes up through the porous bed of feed material into the off-gas system. The air cooled condenser is operated so as to condense an organic phase which contains 15% or less water. A second organic phase is obtained from the draft fan located between the condenser and the after-burner for the noncondensed gases.

The condenser and draft fan wood oils obtained for this study were free flowing liquids and had a dark brownish color and a burnt odor. The water in the

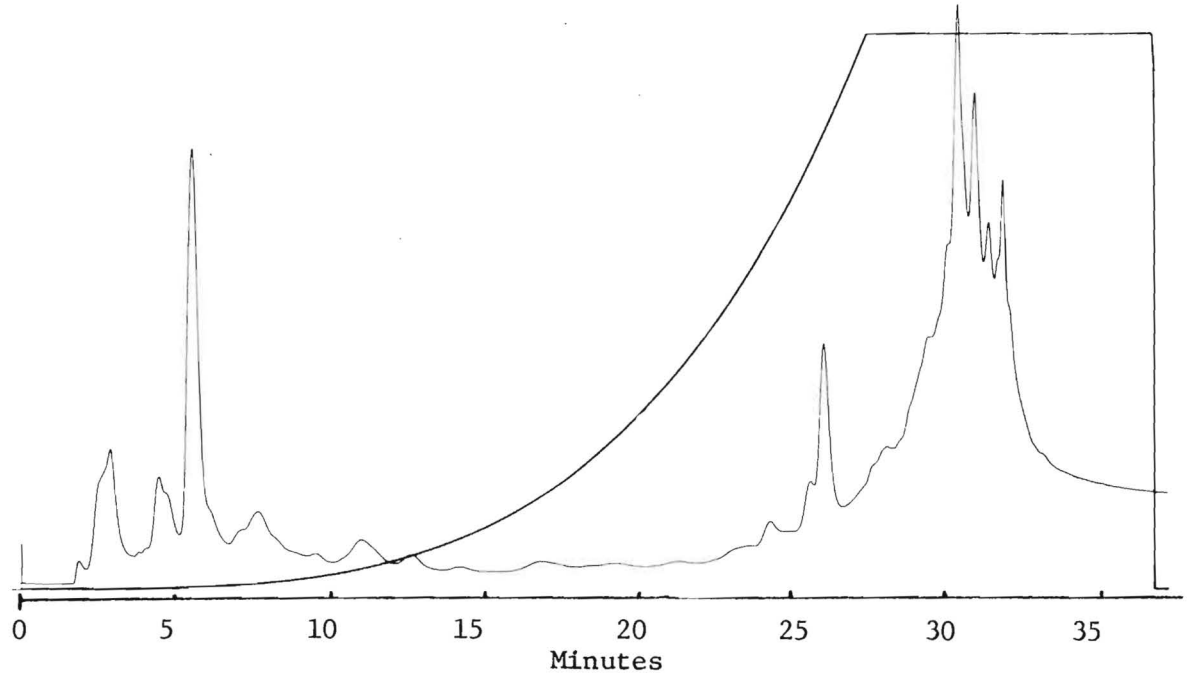

Figure 7. Survey Liquid Chromatogram of Raw Condenser Oil.

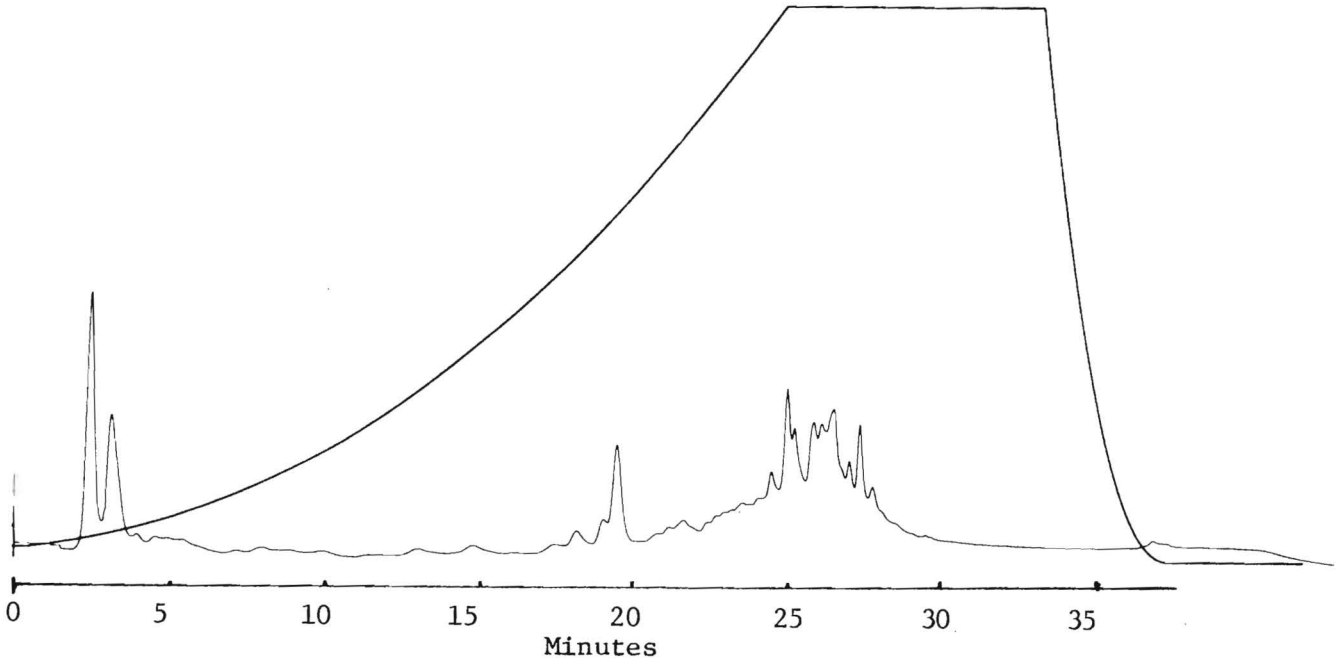

Figure 8. Survey Liquid Chromatogram of Draft Fan Oil.

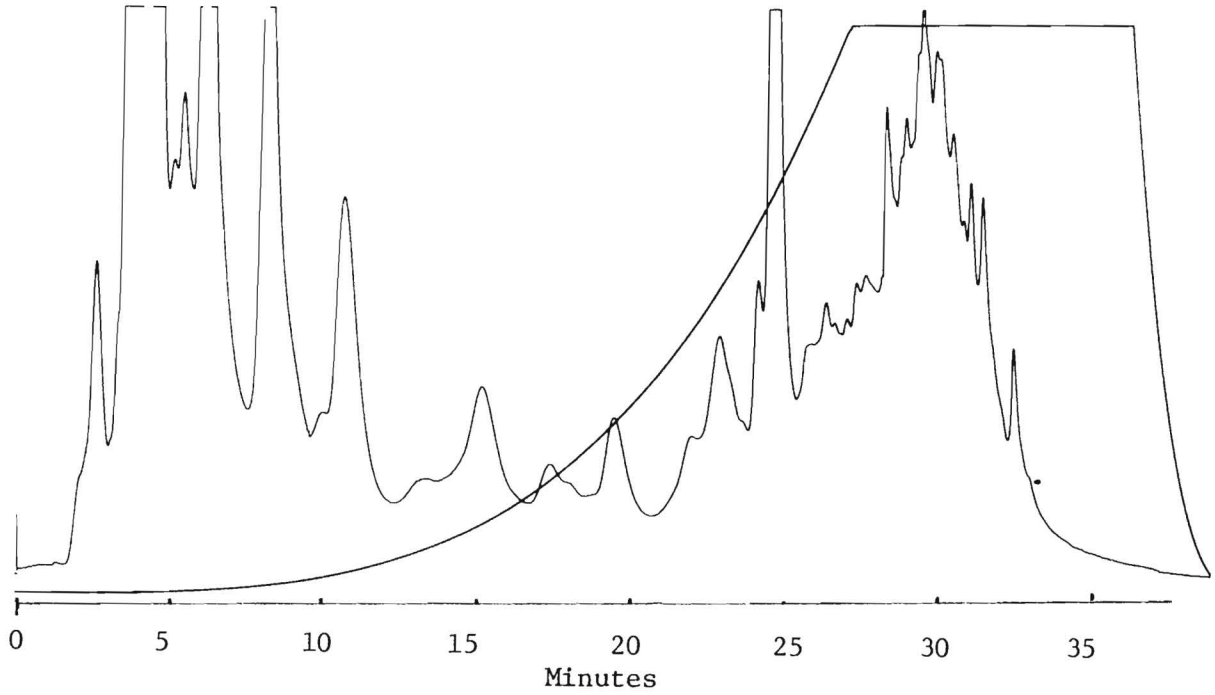

Figure 9. Survey Liquid Chromatogram of Combined Fractions from Vacuum Distillation.

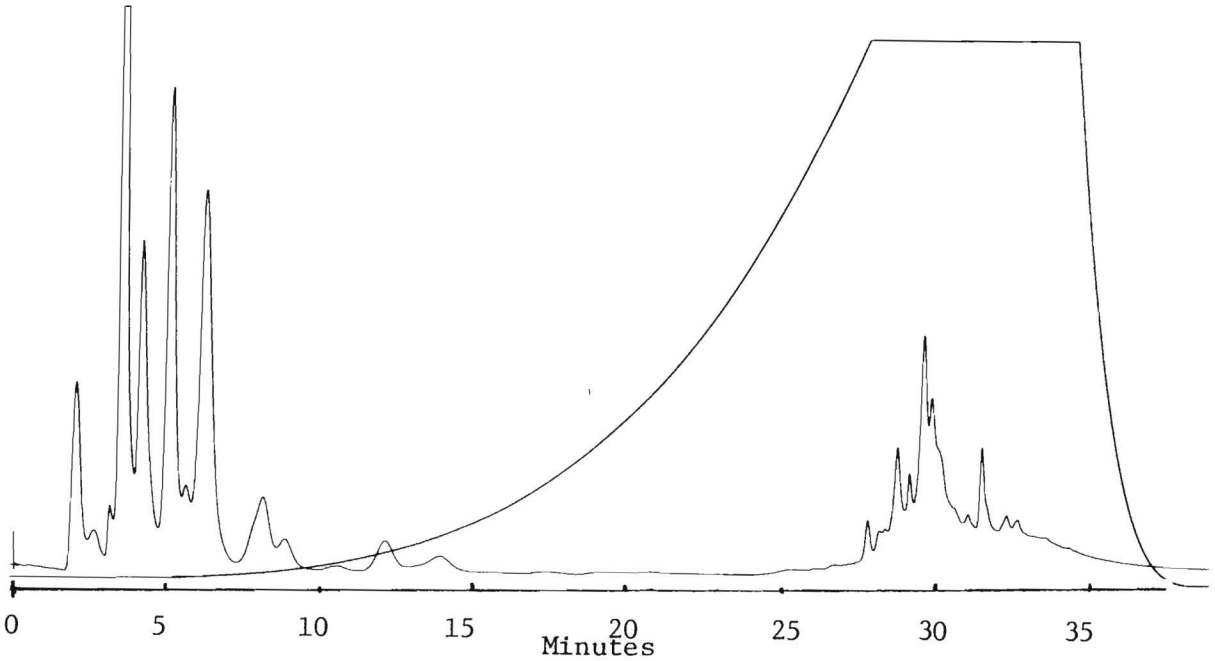

Figure 10. Survey Liquid Chromatogram of Spinning Band 1 Fraction.

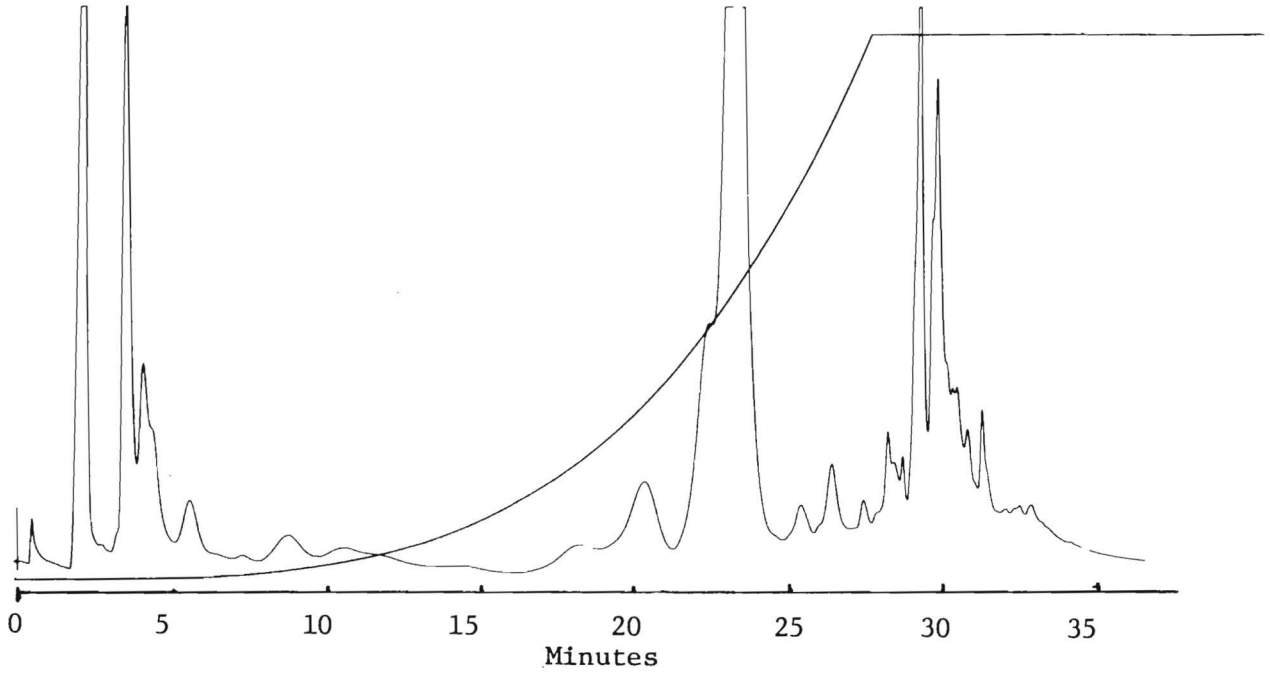

Figure 11. Survey Liquid Chromatogram of Spinning Band 5 Fraction.

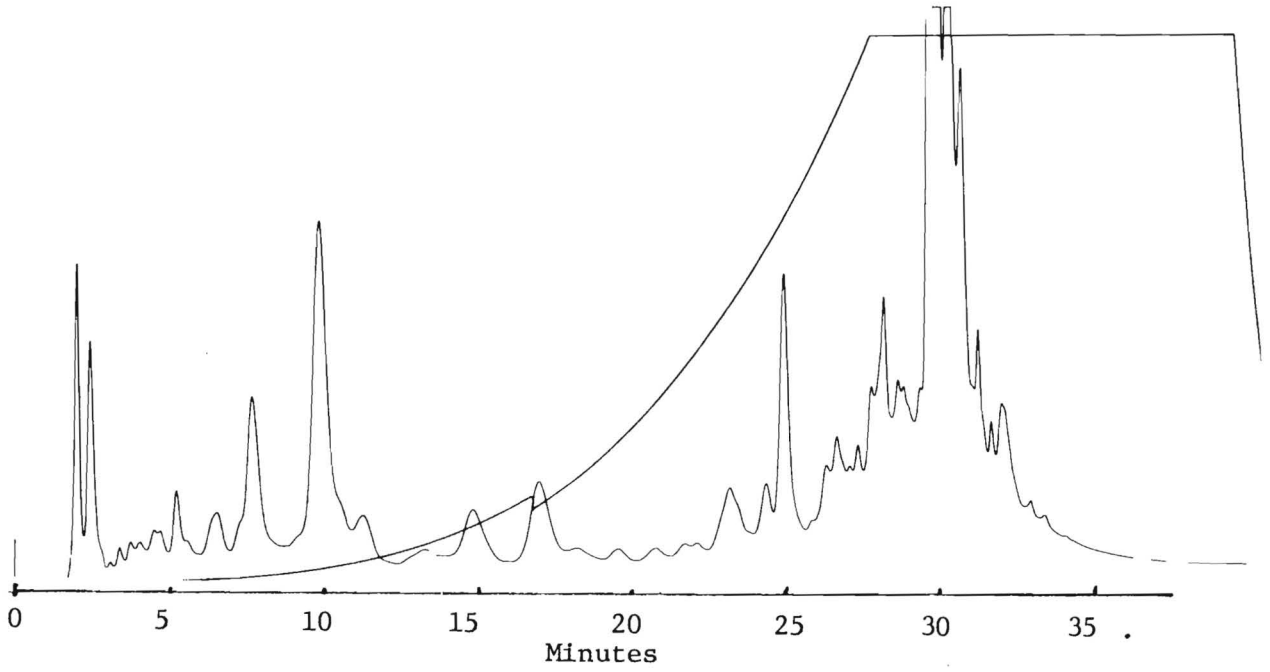

Figure 12. Survey Liquid Chromatogram of Spinning Band 9 Fraction.

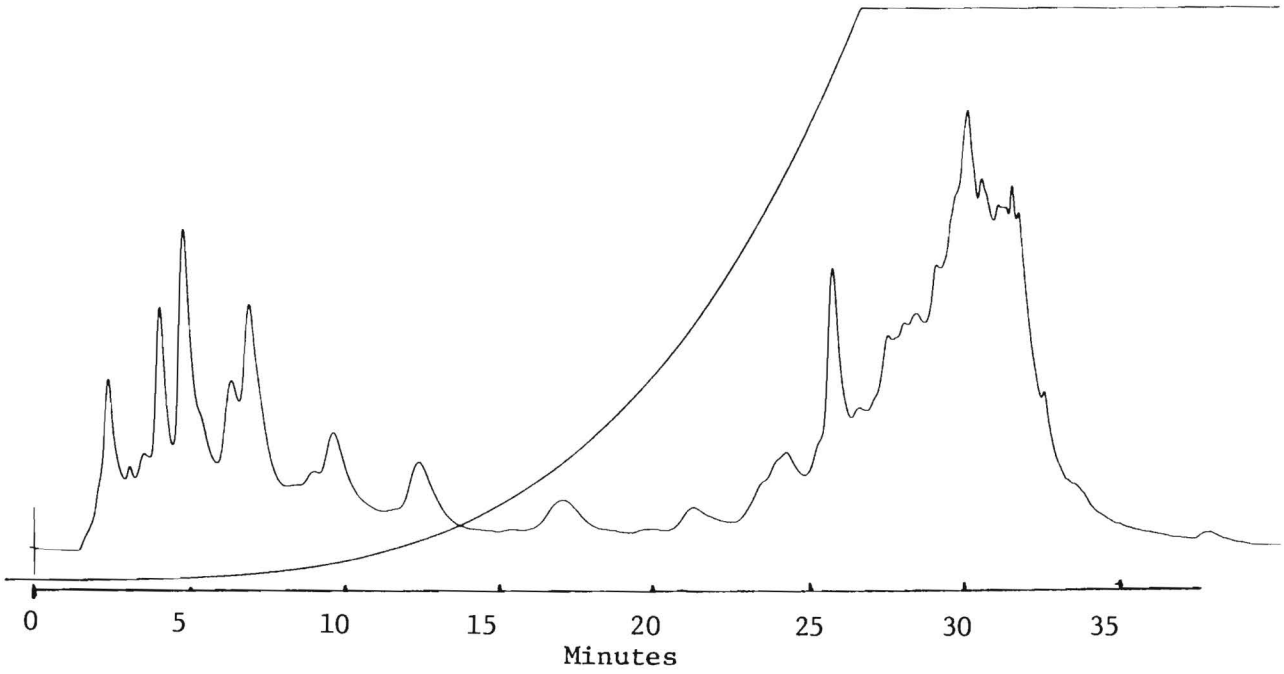

Figure 13. Survey Liquid Chromatogram of Condenser Oil Vacuum Stripped without Heat.

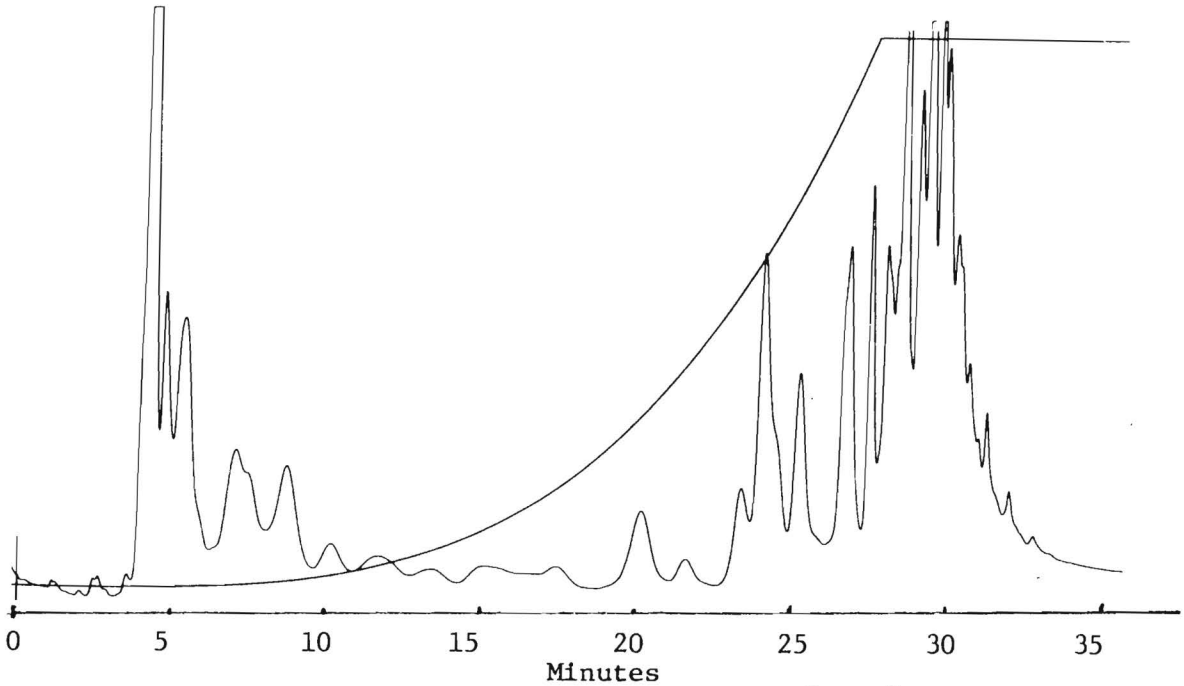

Figure 14. Survey Liquid Chromatogram of 100°-105°C Organic Layer from Steam Distillation.

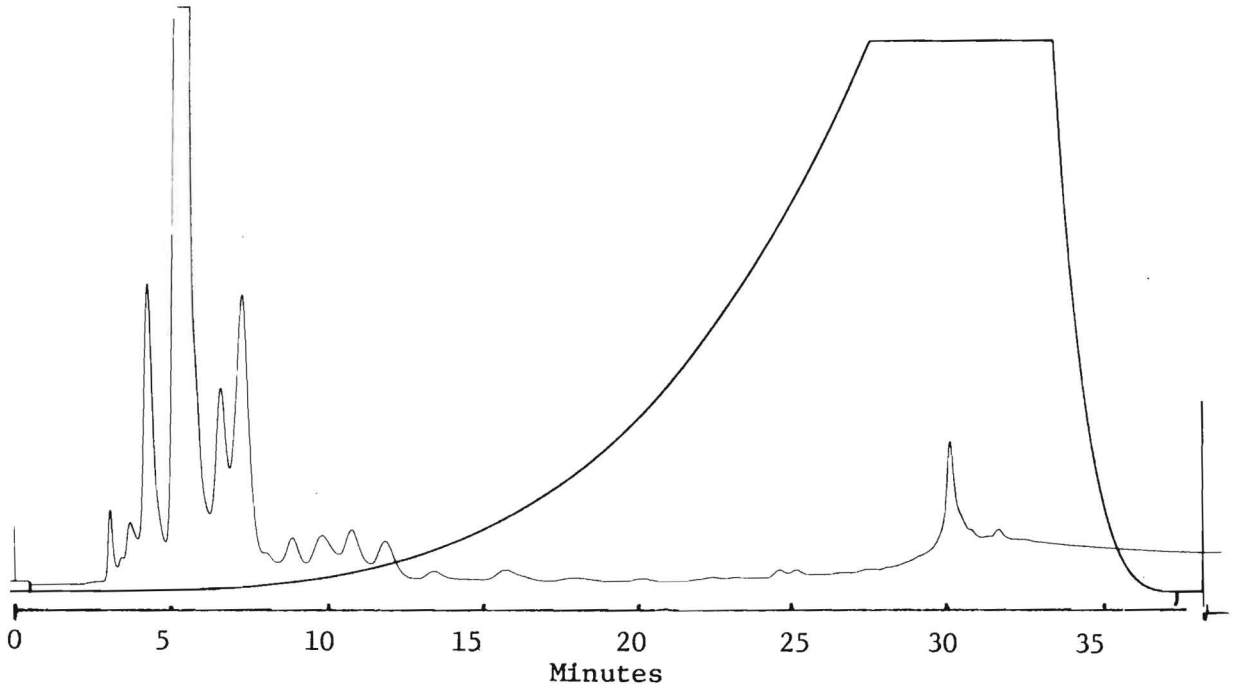

Figure 15. Survey Liquid Chromatogram of 100°-105°C Aqueous Phase from Steam Distillation.

oil is well dispersed or emulsified and does not separate into an aqueous phase on standing. The densities of the oils are greater than water, and the oils are acidic and exhibit some corrosive properties. The heating values of the oils are less than those of fuel oils, since the wood oils contain a fair percentage of oxygen. The properties of samples of the condenser and draft fan oils which were stored for eight months showed some changes (Table III). However, these changes do not appear to be highly significant in the utilization of the oils as fuel.

The wood oils have greater densities than the number 2 and 6 fuel oils. For this reason the heating values of the wood oils are a greater percentage of the heating values of the fuel oils when compared on a volume basis than when compared on a weight basis. The very low sulfur content of these wood oils and similar oils obtained from different lignocellulosic materials is very significant in the use of these oils as fuels. The very low sulfur content means that sulfur emissions will be extremely low when burned. The utilization by blending or cofiring of these types of oils with sulfur containing fuels can be used as a means of reducing sulfur emissions to acceptable levels.

The viscosity of oils is an important property in the handling of these materials. The viscosities of a number of wood oil samples and number 2 and 6 fuels oils were determined and are given in Figures 1 through 6. The viscosities of the wood oils changed some on storage at $0^{o}C$ and ambient temperature over an eight month period. These changes should not have any great effect on the handling characteristics of the oils. The vacuum stripped oils had much higher viscosities at the lower temperatures, but approached the viscosities of the fresh oils at the higher temperatures. These results are essentially what would be expected since the vacuum stripping removes the water in the oils. Sealed samples of the condenser oil were heated at $110^{o}C$ for different time periods, and the viscosity curves are given in Figure 5. The curves show that the viscosity of the heated samples increases markedly with time. The curve for the sample heated 75 hours is very similar to the viscosity curve for number 6 fuel oil. These data show that prolonged heating of oils obtained by pyrolysis must be considered in the material handling of the oils.

A number of distillation experiments were carried out with the condenser wood oil. The data from these initial experiments indicate that distillation

is a potential processing method for obtaining fractions which could have greater utility and value than as a fuel. Additional study is needed on the chemical characteristics of the distillates, however, to find specific uses for them. The wood oils are heat sensitive, and in both atmospheric and vacuum distillation at temperatures of 190°-200°C (head temperature), the material in the flask becomes more viscous and will decompose if heating is continued. It is also of interest that the distillate oil from vacuum distillation of condenser oil exhibited the same behavior when a sample was fractionated in a spinning band column at 0.2-0.4 mm pressure.

Liquid chromatography is an excellent analytical tool for characterization of oils produced by pyrolysis of lignocellulosic materials. Chromatograms on the condenser and draft fan oils and different distillate oils obtained by different distillation techniques show that the oils contain a large number of components. An examination of Figures 10, 11 and 12 for three different fractions of oil obtained from the vacuum fractionation of condenser distillate oil shows that each of these fractions contains a large number of components.

VIII. SUMMARY

The condenser and draft for oils produced by pyrolysis of a pine bark-sawdust mixture is a 50 dry ton/day facility have been characterized and tested by a variety of methods. The oils, as produced, contain approximately 15% or less water, which is well dispersed. The heat values of the oils vary from about 60 to 70% of the heating values of fuel oils on a volume basis. The oils contain essentially no sulfur, and therefore do not create any sulfur emission problems when burned as a fuel. Blending or cofiring with sulfur containing fuels can be used to reduce sulfur emissions to acceptable levels. The tests for oil samples stored eight months at $0^{\circ}C$ and ambient temperature indicate that no significant changes occurred which would affect the use of the oil as a fuel. The oils are acidic and exhibit some corrosive properties. The viscosity of the oils increased with prolonged heating at $110^{\circ}C$, and this factor would have to be considered in the handling of the oil. Also, the oils start to degrade and decompose when heated to approximately $200^{\circ}C$. The oils contain a fair percentage of oxygen and are complex mixtures with a large number of components as shown by liquid chromatographic analysis. It is reasonable to assume that many of the of the components are oxygen containing compounds.

REFERENCES

1. "Conference on Silvilculture Plantations," The Mitre Corporation/Metrek Division and Georgia-Pacific Corporation, Reston, Va., February 15-16, 1977.

2. J. A. Knight, M. D. Bowen, and K. R. Purdy, "Pyrolysis-A Method for Conversion of Forestry Wastes to Useful Fuels: Presented at poster session, Conference-Energy and Wood Products Industry, Forest Products Research Society, Atlanta, Georgia, November 15-17, 1976.

APPENDIX B

EXPENDITURES

June 21, 1976 - May 31, 1977

APPENDIX B

EXPENDITURES

The expenditures from the initiation of the project through May 31, 1977, were as follows:

(a)	Direct wages and salaries	$ 30,487.21
	Retirement (9.1% of applicable wages and salaries)	2,774.34
	Travel	332.10
	Material and Supplies	3,478.64
	Capital	341.63
	Overhead (68% of direct wages and salaries)	20,731.30
	Total	$ 58,145.22
(b)	Total Budget	$ 65,000.00
	Expenditures through January 31, 1977	58,145.22
	Remaining Funds	$ 6,854.78

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

Atlanta, Georgia

Progress Report No. 4

June 1, 1977--September 30, 1977

Project B-469

UTILIZATION AND/OR STABILIZATION OF PYROLYTIC OIL FROM PYROLYSIS OF AGRICULTURAL, MUNICIPAL AND OTHER WASTES

by

J. A. Knight

Grant No. R 804 416 010

Performed for

Municipal Environmental Research Laboratory

Environmental Protection Agency

Cincinnati, Ohio 45268

CONTENTS

SECTION 1

SUMMARY

Three pyrolysis experiments were conducted in our six inch tube pyrolysis system for recovery of all condensible oil and aqueous phases for utilization in our study of pyrolysis oils. Samples of oil were collected also during three different experiments from the operation of our pilot plant pyrolysis system for utilization in our study of pyrolysis oils. Characterization of these oils is currently underway. Steam distillation of a sample of draft fan oil from Tech-Air's Cordele facility was carried out. A technical paper, "Wood Oil from Pyrolysis of Pine Bark-Sawdust Mixture," was presented at the Symposium on Fuels and Energy from Renewable Resources at the fall meeting of the American Chemical Society, August 28--September 2, 1977, in Chicago. The proceedings of the symposium will be published in book form in the near future. The report which covered the work for period June 21, 1976 - May 31, 1977, was completed and submitted. Work on the characterization of pyrolysis oils, with particular emphasis on chemical species, is being continued. Initial plans for bench scale experimental techniques to be tried for separating the oil into more useful fractions were made. The major emphasis during the next work period will be in the investigation of separation techniques to produce fractions of oil. It is anticipated that these oil fractions will have greater potential for specific uses than the raw oil.

SECTION 2

PLANS FOR FUTURE WORK

The emphasis for the next reporting period will be in two areas:

- Extractive and separation techniques will be investigated with the objection of producing fractions from the raw oil which will have greater potential for specific uses than the raw oil.
- Hydrogenation studies of oil samples as a preliminary treatment for the purpose of stablizing the oil.

The approach and objective to separation of the oil into fractions with greater potential value and usefulness is to develop processes of relative simplicity. Also, it is necessary to consider the potential effect of any specific step of an overall process on the final economics of the total system.

In the separation studies, two initial approaches will be investigated. In one approach, water extraction at different temperatures will be used initially. This will be followed by studies with basic solutions of different strengths at different temperatures. The other approach will be an extractive steam distillation of the oil. The pH of the oil-water phase will be varied step-wise from a basic solution to an acidic solution. These initial studies will provide data and results which will be used in to evaluate these approaches and to devise an improved separation process.

Hydrogenation experiments with the oil will be carried out to determine if hydrogenation improves the stability of the oil and if the hydrogenated oil is more amenable to the application of separation techniques as outlined above.

Efforts will be continued on the improvement of techniques for characterization of the oil for evaluation purposes. Particular attention will be given to liquid and gas chromatography.

SECTION 3

EXPERIMENTAL

PYROLYSIS IN TUBE FURNACE

Three pyrolysis experiments were carried out in our six-inch tube furnace with the condensation train. The apparatus is described in Report No. 2, Appendix B, for the October 1, 1976--January 31, 1977, period. In two of the experiments, pine bark-sawdust was used and in the other, hardwood chips were used. In one experiment with pine bark-sawdust, the normal mode of pyrolysis was used. In the normal mode, the tube furnace is operated in such a manner that the heating of the feed material in the tube is started at the opposite end of the outlet for the off-gases. In this manner, the pyrolytic gases and liquids pass from the hotter zone through progressively cooler zones to the outlet tube. In the reverse mode of pyrolysis, the heating of the feed material is started at the end nearest the outlet for the off-gases. In this manner, the pyrolytic gases and liquids pass through progressively hotter zones before reaching the outlet.

Feed Materials

Representative samples of the feed materials were analyzed and the data are given in Table 1.

TABLE 1. PROPERTIES OF FEED MATERIALS

Property	Pine bark-Sawdust	Hardwood Chips	Pine Chips
Moisture %	10.3	8.47	5.48
Heating Value, BTU/lb (dry basis)	9109	8392	9026
Ash	1.3	0.95	0.77

Data for Tube Furnace Pyrolyses

The results of the pyrolysis of the pine bark-sawdust and hardwood chips in the six inch tube furnace are given in Table 2.

TABLE 2. RESULTS OF PYROLYSIS IN SIX INCH TUBE FURNACE

	Pine Bark-Sawdust		Hardwood Chips
	Normal	Reverse	Reverse
Weight of Charge, g	3400	3400	2956
Products			
Char, g	1075	1048	829
Heavy Oil,* g	246	113	158
Light Oil, g	37	47	36
Aqueous Phase,** g	1076	1026	1188
Demister Oil,* g	18	53	67
Gases (liters)	703	868	490
Gases, g by difference	946	1113	678

* Contains dissolved water; ** Contains dissolved organics.

The analytical data obtained to date on the oil and aqueous phases are presented in Table 3.

PYROLYSIS IN ENGINEERING EXPERIMENT STATION PILOT PLANT

The Engineering Experiment Station pyrolysis pilot plant (Blue IV) was operated in a gasification mode with both pine chips and hardwood chips. Advantage was taken of these test runs to collect oil samples for study and utilization on this project. Oil samples were collected at five different points in the off-gas system--one sample each from the three sumps of the condenser, one from the demister and one from the draft fan. The analytical data obtained on these samples of oils are presented in Table 4 for the pine chips and in Table 5 for the hardwood chips.

TABLE 3. ANALYTICAL DATA ON OIL AND AQUEOUS PHASES

Product Property	Pine Bark-Sawdust		Hardwood Chips
	Normal	Reverse	Reverse
Heavy Oil			
Water, %	20.0	14.5	17.6
Heating Value, BTU/lb (wet basis)	11,769	13,017	12,783
Liquid Chromatogram	Yes	Yes	Yes
Gas Chromatogram	Yes	Yes	Yes
Light Oil			
Water, %	0.01	0	0
Heating Value BTU/lb	13,951	15,940	12,436
Liquid Chromatogram	Yes	Yes	Yes
Gas Chromatogram	Yes	Yes	Yes
Aqueous Phase			
Organics, %	10.9	9.7	17
Liquid Chromatogram	Yes	Yes	Yes
Gas Chromatogram	Yes	Yes	Yes

TABLE 4. DATA ON OIL SAMPLES FROM PYROLYSIS OF PINE CHIPS

Oil Sample	Property			
	Water, %	g/ml	Heating Value, BTU/lb	
			Wet Basis	Dry Basis
Condenser				
Sump 1	7.94	1.252	9,905	10,759
Sump 2	22.4	1.214	8,454	10,894
Sump 3	35.0	1.199	7,229	11,121
Demister	18.1	1.217	8,818	10,767
Draft Fan	17.9	1.231	9,314	11,345

TABLE 5. DATA ON OIL SAMPLES FROM PYROLYSIS OF HARDWOOD CHIPS

Oil Sample	Property			
	Water, %	g/ml	Heating Value, BTU/lb	
			Wet Basis	Dry Basis
Condenser				
Sump 1	4.4	1.246	9,946	10,404
Sump 2	18.8	1.204	9,442	11,628
Sump 3	37	1.158	8,528	13,537
Demister	17.4	1.222	8,860	10,726
Draft Fan	14.5	1.199	9,362	10,950

STEAM DISTILLATION

A sample of 173 g of draft fan oil (Cordele, July 1976) which had been stored for about eight months at $0^{\circ}C$ was steam distilled in a manner similar to that reported for the second steam distillation of Cordele condenser oil. This sample had a water content of 15.5%, and the organic portion, therefore, was 146g. The separate oily phase distillate weighed 10g as compared with 7.3g from the condenser oil. The recovered organic material (oily phase distillate plus oily phase remaining flask) was 87% of organic material in original charge. This indicates that 13% of the organic material in the original charge was dissolved in the aqueous phases. The 87% recovery of organic material is this experiment compares favorably with the 87.6% recovery for the steam distillation of Cordele condenser oil.

SECTION 4

REPORT AND TECHNICAL PAPER

The report which covered the experimental work for the period June 21, 1976, through May 31, 1977, was completed and sumbitted to the Environmental Protection Agency.

A technical paper was prepared, "Wood Oil from Pyrolysis of Pine Bark-Sawdust Mixture" by J. A. Knight, D. R. Hurst and L. W. Elston, presented at the Symposium on Fuels and Energy from Renewable Resources at the fall meeting of the American Chemical Society, August 28--September 2, 1977, Chicago. The proceedings of the symposium will be published in book form in the near future. The paper was included in the above report as Appendix A.

SECTION 5

EXPENDITURES

The expenditures from the initiation of the project through September 30, 1977, were as follows:

(a)	Direct wages and salaries	$	39,666.68
	Retirement (9.35% of applicable wages and salaries)		3,490.06
	Travel		745.23
	Material and Supplies		5,914.00
	Capital		341.63
	Overhead (68% of direct wages and salaries)		26,973.34
	Total	$	77,130.94
(b)	Total Budget	$	130,000.00
	Expenditures through September 30, 1977		77,130.94
	Remaining Funds	$	52,869.06

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

Atlanta, Georgia

Progress Report No. 5

October 1, 1977--January 31, 1978

Project B-469

UTILIZATION AND/OR STABILIZATION OF PYROLYTIC OIL FROM PYROLYSIS OF AGRICULTURAL, MUNICIPAL AND OTHER WASTES

by

J. A. Knight

Grant No. R 804 416 010

Performed for

Municipal Environmental Research Laboratory

Environmental Protection Agency

Cincinnati, Ohio 45268

CONTENTS

SECTION 1

SUMMARY

The major emphasis and effort during this report period has been directed toward the development of separation technology for the pyrolysis oils that will yield fractions of oils which will have greater utility as chemical materials and/or feedstocks. A variety of extraction experiments have been carried out with different pyrolysis oils. These experiments include extraction with water at different temperatures, extractive steam distillation, vacuum stripping, and extraction with alkaline solution. Hydrogenation experiments were carried out to obtain some preliminary information on the extent that the pyrolysis oils can be hydrogenated and the effect of hydrogenation on the separation techniques. In addition, analytical techniques for the determination of classes of organic compounds, such as phenolics and acids which are present in the oils, are under development.

The results to date with our studies of separation technology of the oils show that the vacuum stripping of the water of the oils along with the volatiles at ambient temperature is a good step for removal of the acetic acid, which can be recovered from the dilute aqueous solution. Water extraction at different temperatures of the raw oil is a potential second step in a separation procedure. Preliminary experiments with water extractions at 25°C, 50°C and 95°C were carried out on the vacuum stripped oil, and the results from these experiments indicate that water extraction offers an excellent potential step in the separation technology of the oils. For example, water extraction at 25°C of the oils shows that approximately 40% of the oil is water soluble and that this fraction contains all of the acids, approximately 45% of the phenolics in the raw oil, and an organic fraction which has sugar-like characteristics. Vacuum stripping of the oil for removal of the acids, water and other volatiles followed by a water extraction step offers the potential first steps of a separation scheme. Extractive distillation from the initial results does not appear to offer a promising technique for

raw pyrolysis oils. The hydrogenation experiments with the raw oil and vacuum stripped samples show that some hydrogenation does take place. If one assumes a moleculer weight of 200 for the oil, then approximately 0.2 mole of hydrogen is reacted for each mole of oil. The inclusion of a hydrogenation step is the processing of pyrolysis oils would be determined by its overall benefit in relation to the cost. The results from the initial extraction experiments of the raw oils with alkaline solutions indicate that alkaline extraction should not be the initial step in a separation scheme but should be considered for a later step.

Work is in progress on the development of a nonaqueous titration technique for the determination of acids and phenolics in pyrolysis oils and fractions obtained from them. Also, work is continuing with the development of analytical techniques with G.C. and L.C. for the oils and fractions of the oils. Analytical development is a necessary concurrent activity with the separation technology development as it is essential to have good, reliable methods for the determination of the contents of the oils and for evaluation of separation steps.

The results with the separation technology program are very encouraging and indicate that relative simple processes can be developed for separating the oils into a number of fractions which will have potential usefulness as chemicals materials and/or feedstocks.

SECTION 2

PLANS FOR FUTURE WORK

The experimental program for the next report period will be focused and directed toward the development of separation steps for processing pyrolysis oils to produce fractions of the oils which contain a large concentration of a class of organic compounds, such as phenolics. The emphasis will be on the development of relative simple separation steps.

In the separation technology area, the water extraction experiments will be continued with the oils, both raw and hydrogenated. Some preliminary experiments using water with dissolved salt will be carried out to test the salt water as an extraction solution. The utilization of organic solvents will be tested in some extraction experiments.

Efforts will be continued on the development of techniques for characterization of the oils and oil fractions for evaluation and assessment of the separation steps.

SECTION 3

EXPERIMENTAL

SEPARATION TECHNIQUES

Water Extraction of Pyrolysis Oil

The oils produced by the continuous pyrolysis of forestry residues in the EES pyrolysis system usually contain approximately 15% water which does not separate on standing. Also, the oils contain highly polar compounds which should show varying degrees of water solubility. Some preliminary extraction experiments of Cordele oil (July, 1976 oil) were carried out with water at different temperatures to determine the feasibility of water extraction as a step in the processing of pyrolysis wood oils.

In the first experiment the oil was extracted with water at 25°C followed by extraction with water at 95°C, and the schematic for this experiment is shown in Figure 1 .

In the second experiment the oil was extracted with water at 50°C followed by extraction with water at 95°C, and the schematic for this experiment is show in Figure 2 . The distribution of the organic acids and phenolic substances as determined by a nonaqueous titration technique is given in Table 1 .

TABLE 1. DISTRIBUTION OF ACIDS AND PHENOLICS FROM WATER EXTRACTION EXPERIMENTS

	Experiment 1		Experiment 2	
Sample	Acids	Phenolics	Acids	Phenolics
Cordele Oil	9.6g	8g	9.6g	8g
Water, 25°C	4.6g	1.1g	--	--
Water, 50°C	--	--	10.9g	4.1g
Water, 95°C	3.8g	1.9g	0.2g	2.5g
Insoluble Oil Residue	1.0g	5.5g	0	1.3g

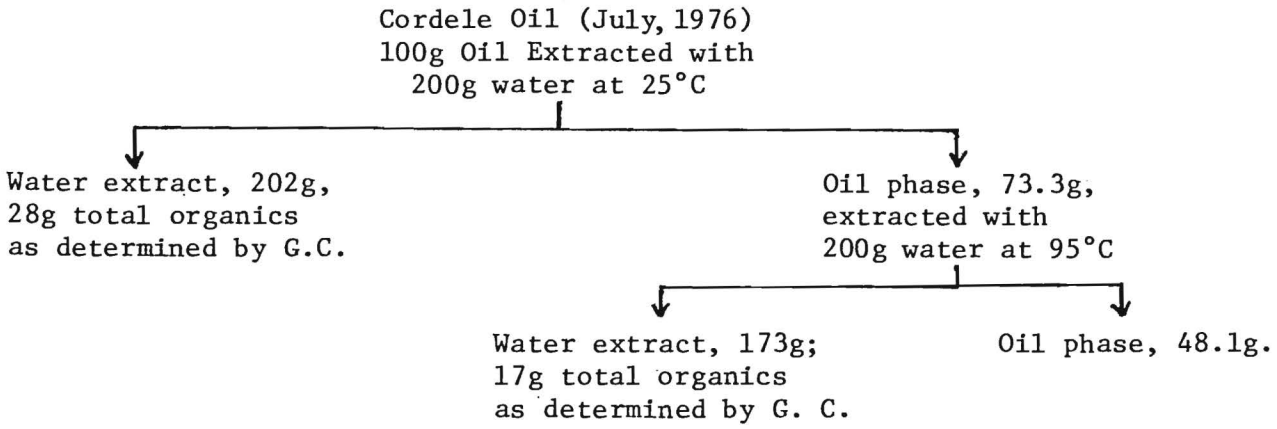

Figure 1. Water Extraction No. One of Pyrolysis Oil

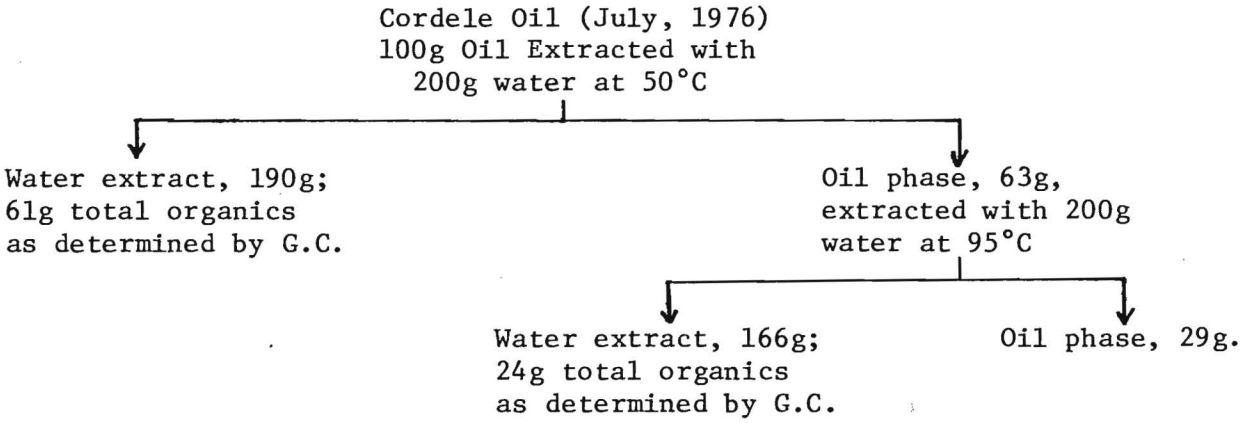

Figure 2. Water Extraction No. Two of Pyrolysis Oil

A third extraction experiment with water at different temperatures was carried out with draft fan pine oil produced in the EES Blue IV pyrolysis pilot plant. This oil was produced in July, 1977, from pine chips and had approximately 18.5 percent phenolic content as determined by nonaqueous titration. The oil was extracted with water at 25°C, 50°C and 95°C. The results from these extractions are given in Table 2, and show that with this oil, the acids are extracted completely with the 25°C water. The results indicate that approximately 50% of the phenolic substances can be extracted with water extractions at 25°C and 50°C and that about 24 percent was not extracted with water. The results also show that at 25°C approximately 22 percent of the organic content of the original oil was extracted with 25°C water. Preliminary results indicate that this is a sugar-like material.

TABLE 2. RESULTS FROM WATER EXTRACTION OF DRAFT FAN PINE OIL

	Extracted Materials		
Sample	Acids	Phenolics	Other
Original Oil	5.4g	18.5g	59.1g
Water Extract, 25°C	5.9g	6.7g	18.3g
Water Extract, 50°C	0	2.7g	0.6g
Water Extract, 95°C	0	0.6g	0.2g
Water Insoluble Oil	0	4.5g	19.6g

Extractive Steam Distillation

A sample of Cordele condenser oil (July, 1976) was distilled in the following manner to obtain preliminary data about the feasibility of separating fractions of the oil by distillations from a solution using different acidic and basic conditions. In step one, a mixture of oil and basic solution of pH>10 was distilled to yield an oil phase lighter than water and an aqueous phase. In step 2, the pH was adjusted to an acidity of between 3 and 7, and distilled to yield an oil phase heavier than water and an aqueous phase. In step three, the

acidity was adjusted to a pH less than one and distilled to yield a turbid aqueous phase with no separate oil phase. The yields of this experiment are given in Table 3 . The oil phase from step one had a decided pyridine odor. The analyses of both the oil and aqueous phases from step one did not indicate the presence of any organic acids or phenolics. The oil phase from step two was approximately 41% phenolics with no organic acids. The analysis of the aqueous phase from step two indicated that phenolics were not present.

TABLE 3. YIELDS FROM EXTRACTIVE STEAM DISTILLATION

Step No.	Oil Phase	Aqueous Phase	
		Organics	Water
1, pH>10	1.5g	101.1g	140.3g
2, pH>3 ≤7	6.5g	33.7g	120.8g
3, pH<1	0	18.8g	153.7g

Alkaline Extraction of Pyrolysis Oils

Some preliminary work was carried out on the extraction of two different pyrolysis oils with five percent sodium hydroxide solution to determine the reactions of the oils to basic solutions. A 50g sample of draft fan pine oil was treated with 200ml of the five percent sodium hydroxide solution. The organic material went into solution and was easily filtered, leaving only a trace of char. The experiment was repeated with draft fan hardwood oil. With the hardwood oil, some dissolved leaving a black tarry material, which was soluble in absolute ethanol, but insoluble in methylene chloride.

Vacuum Stripping of Pyrolysis Oils

Samples of pyrolysis oils from different sources were needed from which the water had been removed under mild conditions. Previous experience had shown that this could be accomplished by stripping off the water along with volatile organics at ambient temperature at a pressure of approximately 0.2 mm. Heating of the flask to speed up the stripping operation was avoided because of the heat sensitivity of the pyrolysis oils. A description of the process is given in

Report No. 3, February 1, 1977--May 31, 1977. The results with five different oil samples is given in Table 4 .

TABLE 4. VACUUM STRIPPING OF PYROLYSIS OILS

Oil Sample	% Weight Loss*	% Weight of Recovered Condensates*	% Water by Dean-Stark Method
Cordele Condenser Oil	19.5	18.2	19.5
Blue IV Hardwood Composit Oil	10.3	11.2	12.8
Blue IV Fan Hardwood Oil	11.4	12.6	12.8
Blue IV Pine Composite Oil	14.9	14.9	17.8
Blue IV Fan Pine Oil	14.1	14.3	17.8

*Based on original weights of oil samples.

These data indicate that the removal of the water along with volatile organics is a more difficult process with the oil from pine feedstock than from hardwood. The data also indiciate it is very difficult to remove the last traces of water from pyrolysis oil samples by vacuum stripping. The data indicate that the pine oil samples contained approximately three percent water after the stripping operation, whereas the hardwood composite oil sample contained 1.6% water. These samples were needed for some preliminary hydrogenation experiments and were adequate for these tests.

HYDROGENATION

Oil samples from different sources were hydrogenated catalytically to determine how much hydrogentation would occur and the effect of hydrogenation on the stability of the oil and to prepare samples for use in various separation schemes. Hydrogenation were carried out in a Parr Model 3911 hydrogenation apparatus which provides for agitation by shaking and can be used at pressures up

to approximately 20 atmospheres. One hydrogenation was conducted at atmospheric pressure utilizing a recycling of the hydrogen in a stirred flask containing the sample and catalyst. Anhydrous ethanol was used as a solvent, and five percent palladium on activated carbon or five percent platinum on activated carbon was used a catalyst. The results from the hydrogenations with low pressure Parr apparatus and at atmospheric pressure are given in Table 5 .

The data from hydrogenations 5, 6 and 7 show that the Pd catalyst performs better as the hydrogen adsorbed is approximately fifty percent greater in one-third of the time used for the hydrogenations with Pt. The data from hydrogenation 4 show that hydrogenation at atmospheric pressure is too slow. Examination of the data from hydrogenations 5, 8 and 9 show that the Blue IV fan oil from both hardwood and pine chips absorbed approximately the same amount of hydrogen under similar conditions, whereas the Blue IV composite hardwood oil adsorbed 2.2 times as much hydrogen as the Blue IV composite pine oil. It is of interest that the vacuum stripped hardwood oil, hydrogenation 11, absorbed 1.56 as much hydrogen as the vacuum stipped pine oil, hydrogenation 10.

Hydrogenations are frequently carried out at a much higher pressure than those discussed above. In order to test a higher initial hydrogen pressure, a Parr Model 1108 calorimeter bomb was connected to a high pressure hydrogen reservoir (lecture bottle size) utilizing a Parr oxygen bomb filter hose assembly and stainless steel tubing. Agitation was provided by means of a magnetic stirrer. Three hydrogenations were carried out with this apparatus with vacuum stripped Blue IV fan pine oil. In each hydrogenation, two grams of five percent palladium on activated carbon and 100 ml of absolute ethanol were used. The hydrogenated oil was recovered by removal of the catalyst by filtration and then vacuum stripping of the ethanol at 2 mm pressure. The results of these three hydrogenations are given Table 6 . An examination of the data show that the hydrogen absorption is the same for each experiment and that the samples absorbed approximately seventeen percent more hydrogen than the same sample at approximately 4 atmospheres (hydrogenation 10 Table 5).

TABLE 5. HYDROGENATIONS AT MODERATE PRESSURE*

No.	Sample Source	Weight g	Water %	Weight "dry" oil†	Initial pressure, psig	Time hrs.	H_2 Aborsbed mg/g on "dry" basis
1.	Cordele Condenser Oil	32.2	19.5	26.0	55.2	18	1.4
2.	Blue IV Hardwood Composite Oil	20.8	12.8	18.1	55.5	20	4.9
3.	Blue IV Pine Composite Oil	24.1	17.8	19.8	56.0	26	2.2
4.	Blue IV Fan Hardwood Oil‡	65.1	12.4	57.0	Ambient pressure	60	1.1
5.	Blue IV Fan Hardwood Oil	54.0	12.4	47.3	55.1	22	27
6.	Blue IV Fan Hardwood Oil	52.1	12.4	45.6	55.3	72	1.9
7.	Blue IV Fan Hardwood Oil	68.8	12.4	60.3	56.2	72	1.4
8.	Blue IV Fan Pine Oil	45.9	17.9	37.7	57.2	24	2.4
9.	Blue IV Fan Pine Oil	56.9	17.9	46.7	57.1	24	2.4
10.	Blue IV Fan Pine Oil, Vaccum Stripped	34.4	0	34.4	58.1	26	1.8
11.	Blue IV Fan Hardwood Oil, Vaccum Stripped	59.0	0	59.0	59.0	60	2.8

* 5% Pd on activated carbon was used in all experiments except 6 and 7, in which 5% Pt on activated carbon was used. Two grams of catalyst were used in each experiment. Approximately 200 ml of absolute ethanol was used for each hydrogenation.

† Calculated dry weight of oil based on percent water.

‡ This experiment was conducted in the recycle apparatus at ambient pressure.

TABLE 6. HYDROGENATIONS AT INTERMEDIATE PRESSURES

No.	Sample Source	Initial Pressure Atmospheres	H_2 Absorbed mg/g
12.	Blue IV Fan Pine Oil	18.0	2.1
13.	Blue IV Fan Pine Oil	19.5	2.1
14.	Blue IV Fan Pine Oil	20.0	2.1

ANALYTICAL

Analysis of Pyrolysis Oils for Phenolic and Carboxylic Acid Content

The analysis of pyrolysis oils and fractions of pyrolysis oils produced by separation processes is extremely important in the research and development of processes designed to produce fractions of the oils of greater utility and value. Data are needed on the raw pyrolysis oils on the quantities of various chemical species in the oil. These data are helpful in the design of separation schemes. Data are also essential on the quantities of chemical species present in fractions obtained from the oils so that the effectiveness and efficiencies of the processes can be evaluated. For these purposes, analytical methods are needed which are reliable, relative simple and can be preformed in a short period time.

Analytical data indicate that a reasonable quantity of phenolic compounds are present in most pyrolysis oils. This class of compounds is particularly interesting because of the potential utilization of the phenolic fraction from pyrolysis oils in resins and similar materials. A survey of the literature revealed an ASTM procedure* which might be applicable. This procedure is used in the determination of the apparent free phenols in synthetic phenolic resins or solutions used for coating purposes. In this method, the free phenols are isolated by steam distillation and then titrated iodimetrically. The procedure was tested with eleven different samples of pyrolysis oils and was found to

* ASTM D1312-56, Method B.

produce results which were totally unreliable and/or unrealistic.

The literature survey also suggested that nonaqueous titrations offered a possible approach for determining both the phenolic and carboxylic acid contents of pyrolysis oils. A nonaqueous titration procedure has been developed which yields results with pyrolysis oils that are apparently reliable and realistic. The nonaqueous titration procedure was developed with know phenolic compounds and then applied to pyrolysis oil samples. For the purposes of this program, the results indicate that the procedure is adequate. Simultaneously, efforts are in progress to develop analytical techniques for the phenolic content utilizing G.C. and L.C. The nonaqueous titration technique was used to analyze samples reported in the section on separation techniques.

G.C. Analysis of Aqueous and Alcoholic Condensates

Samples of the aqueous condensates from the vacuum stripping of oil samples and of the alcoholic condensates from the hydrogentation experiments were analyzed by G.C. for organic content. In the case of the alcoholic condensates, the samples were analyzed for organic compounds other than ethyl alcohol. The gas chromatograms from these preliminary experiments showed the presence of acetic acid as the major organic compound in the condensates. Examination of the chromatograms showed the presence of three or four unknown peaks in very low concentrations in the aqueous condensates. The data from these analyses are presented in Tables 7 and 8 .

TABLE 7. G.C. ANALYSIS OF AQUEOUS CONDENSATES FROM VACUUM STRIPPING

Sample Source	% Acetic Acid*
Blue IV Pine Composite Oil	5.0
Blue IV Fan Pine Oil	7.1
Blue IV Fan Hardwood Oil	15.2

* Based on weight of aqueous condensates.

TABLE 8 . G.C. ANALYSIS OF ALCOHOLIC CONDENSATES FROM HYDROGENATIONS

Sample Source	% Acetic Acid*
Blue IV Fan Hardwood Oil†	0.14
Blue IV Fan Hardwood Oil†	0.26
Blue IV Fan Hardwood Oil†	0.18
Blue IV Fan Hardwood Oil, Vacuum Stripped	0.23
Blue IV Fan Pine Oil†	0.46
Blue IV Fan Pine Oil, Vacuum Stripped	0.08

* Based on weight of alcoholic condensates.
† Hardwood oil, 12.8% water; pine oil, 17.8% water.

These preliminary data indicate that the major compound to be considered for recovered from aqueous condensate from vacuum stripping in the processing of pyrolysis oils is acetic acid and that the quantity of acid varies with the species of wood. The data also show that some acetic acid is present in the vacuum stripped oil and is potentially recoverable from the alcoholic condensates.

SECTION 4

PUBLICATION

A technical paper, "Wood Oil from Pyrolysis of Pine Bark-Sawdust Mixture" by J. A. Knight, D. R. Hurst and L. W. Elston, was presented at the Symposium on Fuels and Energy from Renewable Resources at the fall meeting of the American Chemical Society, August 28--September 2, 1977, Chicago. The proceedings of this symposium were published in book form in December, 1977. A reprint of this publication is presented in Appendix A.

APPENDICES

APPENDIX A

Publication

"Wood Oil from Pyrolysis of Pine Bark-Sawdust Mixture"

J. A. Knight
D. R. Hurst
L. W. Elston

Presented at

American Chemical Society
Chicago, Ill.

August 28-September 2, 1977

Published
in
"Fuels and Energy from Renewable Resources"
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APPENDIX B

EXPENDITURES

June 21, 1976-January 31, 1978

FUELS AND ENERGY FROM RENEWABLE RESOURCES

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CONTENTS

WOOD OIL FROM PYROLYSIS OF PINE BARK-SAWDUST MIXTURE*

J. A. Knight, D. R. Hurst, and L. W. Elston

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I. INTRODUCTION

Pyrolysis has received considerable attention in the last several years as a method for converting waste materials--agricultural, silvicultural, and municipal refuse--into useful products, particularly fuels; and at the same time, serving as a satisfactory disposal method. Pyrolysis is now receiving consideration as a process for the conversion of biomass from biomass plantations into useful products, particularly fuels [1]. Pyrolysis of lignocellulosic materials produces a char, condensible organic substance, water, and noncondensible gases. The char and condensible organic liquid can be utilized as clean burning fuels, and the noncondensed gas is a low Btu fuel that must be used on site.

* Supported in part by E.P.A. Grant No. R804 416 010.

Workers at the Engineering Experiment Station (EES) have found that pyrolysis is readily adaptable for the conversion of a variety of cellulosic and lignocellulosic materials into useful fuels and other products. During the past eight years, a steady flow, low temperature pyrolysis system has been developed which involves processing of the feed material in a continuous operation in a porous, vertical bed [2]. The Tech-Air Corporation, Atlanta, licensee for the process, has successfully operated a 50 dry ton/day field demonstration pyrolysis facility at a lumber yard at Cordele, Georgia. The feed material utilized at this facility is a mixture of pine bark and sawdust.

The physical and chemical characteristics obtained from the pyrolysis of various types of waste materials are needed for the proper evaluation and utilization of these oils. These data are also useful in establishing the pyrolysis operating conditions for production of the most suitable oils. There are many available testing and characterization procedures that have been developed for petroleum, vegetable, and other oils. Some of these, or modifications, will prove useful for oils obtained by pyrolysis of lignocellulosic wastes. The data presented below were obtained on wood oils produced in the Tech-Air facility.

II. WOOD OIL SAMPLES

Approximately 110 gallons of oil for this study were collected on July 15, 1976, at the facility while it was operating in a steady state mode. Approximately equal quantities of oil were obtained from the air cooled condenser and the draft fan, which is located between the condenser and the after-burner for the noncondensed gases. Samples of both oils were stored at ambient temperature and 0°C for future characterization and use. A representative sample of the feed material, a mixture of pine bark-sawdust, had the chararacteristics and properties as listed

in Table I, and the results of the characterization and analyses of representative samples of both oils are given in Table II.

Certain properties were redetermined on samples of the oil, which had been stored at 0°C and ambient temperatures for approximately eight months. These results, along with the initial values, are given in Table III.

One significant use of these oils is as a fuel. Therefore, it is of interest to compare some typical properties of the condenser and draft fan wood oils with #2 and #6 fuel oils. These values are given in Table IV. Because of the greater densities of the wood oils, the heating values of the wood oils when compared on a volume basis are larger percentages of the heating values of the fuels oils than when compared on a weight basis. The very low sulfur content of the wood oils is a significant property for the utilization of these materials as fuels. Proper blending of wood oils with high sulfur fuel oils can serve as a means of reducing the overall sulfur content of the combined fuel, and consequently, sulfur emissions.

TABLE I. Properties of Pine Bark-Sawdust Feed Material

Property	*Result*	*Method*
Pine bark *Pine sawdust*	*70%* *30%*	*Microseparation by visual means*
Bulk density	*21.3 kg/cu m* *13.3 lbs/cu ft*	
Moisture	*10.3%*	*ASTM D-1762-64*
Ash (weight %)	*1.3%*	*ASTM D-1762-64*
Acid insoluble ash (weight %)	*<0.1%*	
Heating value (dry basis)	*5061 cal/g* *9109 Btu/lb*	*ASTM D-240-74*

TABLE II. Properties of Wood Oils From Tech-Air 50 Dry Ton/Day Facility

Property	Condenser Oil	Draft Fan Oil	Method
Density	1.1415 g/ml 9.525 lbs/gal	1.1075 g/ml 9.242 lbs/gal	-
Water content (weight %)	14.0%	10.4%	ASTM D 95-70
Heating value (wet basis)	5,056 cal/g 9,100 Btu/lb	5,883 cal/g 10,590 Btu/lb	ASTM D 240-64
pH	2.9	3.3	5% oil dispersed in water
Acid number	75 mg KOH/g	31 mg KOH/g	ASTM D-664-58
Flash point	111°C 233°F	121°C 240°F	ASTM D-93-73
Filterable solids (weight %)	0.3%	0.4%	Acetone insoluble
Copper strip corrosion	1	1	Classification ASTM D-130-7
Sulfur (weight %)	<0.01%	<0.01%	ASTM D-129-64
Pour point	26.7°C 80°F	26.7°C 80°F	ASTM D-97-66
Ash (weight %)	0.08%	0.03%	-
Distillation			ASTM D-86 Group 3
First drop	98°C	101°C	
10% point	103°C	105°C	
48% endpoint	NA	265°C	
53% endpoint	282°C	NA	
Solubility (weight %)			
Acetone	99.6%	99.6%	
Methylene chloride	93.5%	97.8%	
Toluene	Slightly	Slightly	
Hexane	Slightly	Slightly	
Elemental analysis (weight %)			
Carbon	51.2	65.6	
Hydrogen	7.6	7.8	
Nitrogen	0.8	0.9	

TABLE III. Variation of Oil Properties Over Eight Months Period

Property	Condenser oil		
	Initial value	Stored eight months	
		0°C	Ambient temperature.
Water content (weight %)	14.0%	20.5%	24.1%
Heating value (wet basis)	5,056 cal/g 9,100 Btu/lb	5,444 cal/g 9,800 Btu/lb	5,106 cal/g 9,190 Btu/lb
Acid number	75 mg KOH/g	87 mg KOH/g	89 mg KOH/g
Viscosity[a]	275 cP	350 cP	175 cP
pH	2.6	3.4	2.9

Property	Draft fan oil		
	Initial Value	Stored eight months	
		0°C	Ambient temperature
Water content (weight %)	10.4%	15.5%	12.7%
Heating value (wet basis)	5,883 cal/g 10,590 Btu/lb	5,922 cal/g 10,660 Btu/lb	5,939 cal/g 10,690 Btu/lb
Acid number	31 mg KOH/g	71 mg KOH/g	60 mg KOH/g
Viscosity[a]	233 cP	79 cP	475 cP
pH	3.3	3.1	3.0

a. Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25°C at 60r/min.

TABLE IV. Typical Properties of Wood Oils and Fuel Oils

	Wood oils[a]		Fuel oils[b]	
Property	Condenser	Draft fan	#2	#6
Water content, %	14	10.4	Trace	2
Btu/lb	9,100	10,590	19,630	18,590
Btu/gal	86,700	97,850	139,400	148,900
Density, g/ml	1.142	1.108	0.851	0.960
Lb/gal	9.53	9.25	7.10	8.01
Pour point	80°F	80°F	0°max	65-85°F
Flash point	233°F	240°F	100°F min	150°F
Viscosity, cP[c]	225	233	20	2262
Elemental analysis				
Carbon %	51.2	65.6	86.1	87.0
Hydrogen %	7.6	7.8	13.2	11.7
Nitrogen	0.8	0.9	-	-
Sulfur %	<0.01	<0.01	0.6-0.8	0.9-2.3

a. Values obtained on oils with moisture content as reported.

b. Values for fuel oils are considered typical. Sulfur will vary depending origin of oil. Ref.: North American Combustion Handbook, lst ed., North American Mfg. Co., Cleveland, Ohio, 1952.

c. Determined with Brookfield Viscosimeter, Model LV with Thermosel system at 25°C at 60r/min.

III. VISCOSITY

The viscosity of liquids and its change with temperature is a significant property, particularly with liquids that will be handled by pumping. The viscosity values for the wood oils in this study were determined with a Brookfield viscosimeter, Model LV, with Thermosel system. The viscosity versus temperature was determined for both the condenser and draft fan oils initially and on samples which had been stored at 0°C and ambient temperature for approximately eight months. These viscosity curves are given in Figs. 1 and 2. The viscosity versus temperatures curves of samples of both oils which had been vacuum stripped for removal of water, as described in Section IV E, are given in Figs. 3 and 4. In order to determine the effect of prolonged heat upon the viscosity of condenser oil, samples of sealed oil were heated at 110°C for different time periods, and the viscosity was then determined for each sample. These data are presented in Fig. 5. For comparison, the viscosities of the condenser oil and #2 and #6 fuel oils are presented in Fig. 6.

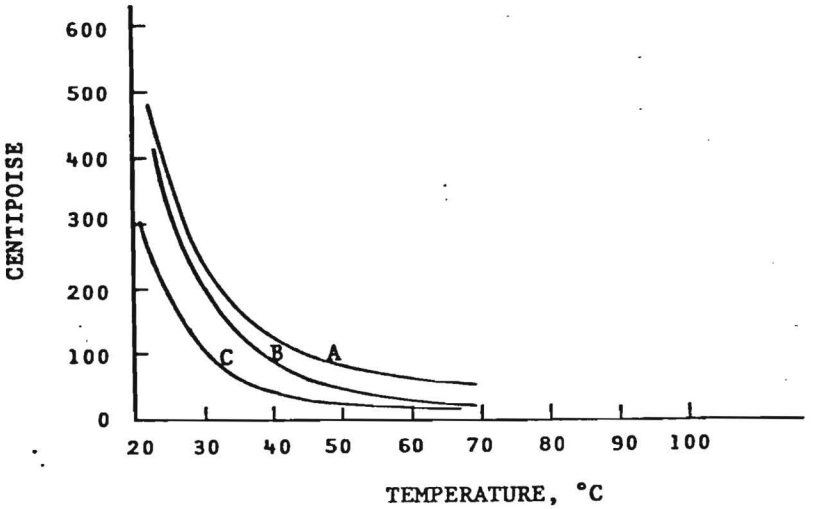

FIGURE 1. Viscosity of condenser oil: (A) Initial viscosity curve; (B) sample stored at 0°C for eight months; and (C) sample stored at ambient temperature for eight months.

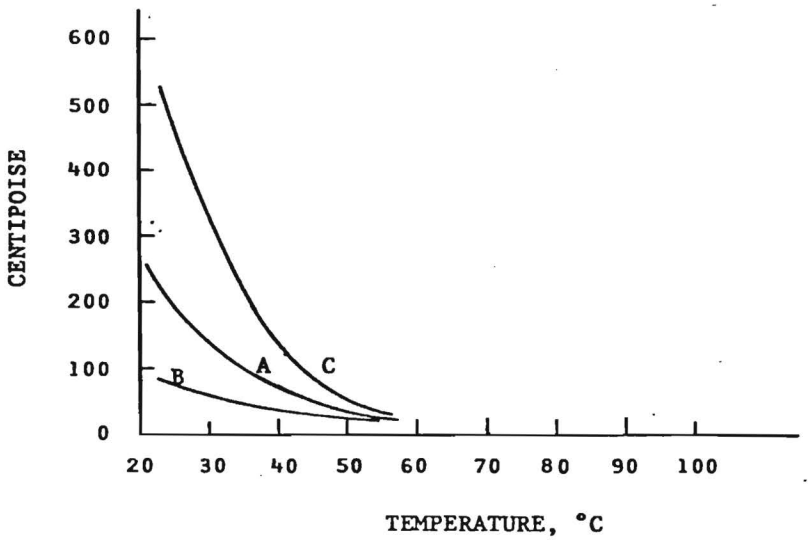

FIGURE 2. Viscosity of draft fan oil: (A) Initial viscosity curve; (B) sample stored at 0°C for eight months; and (C) sample stored at ambient temperature for eight months.

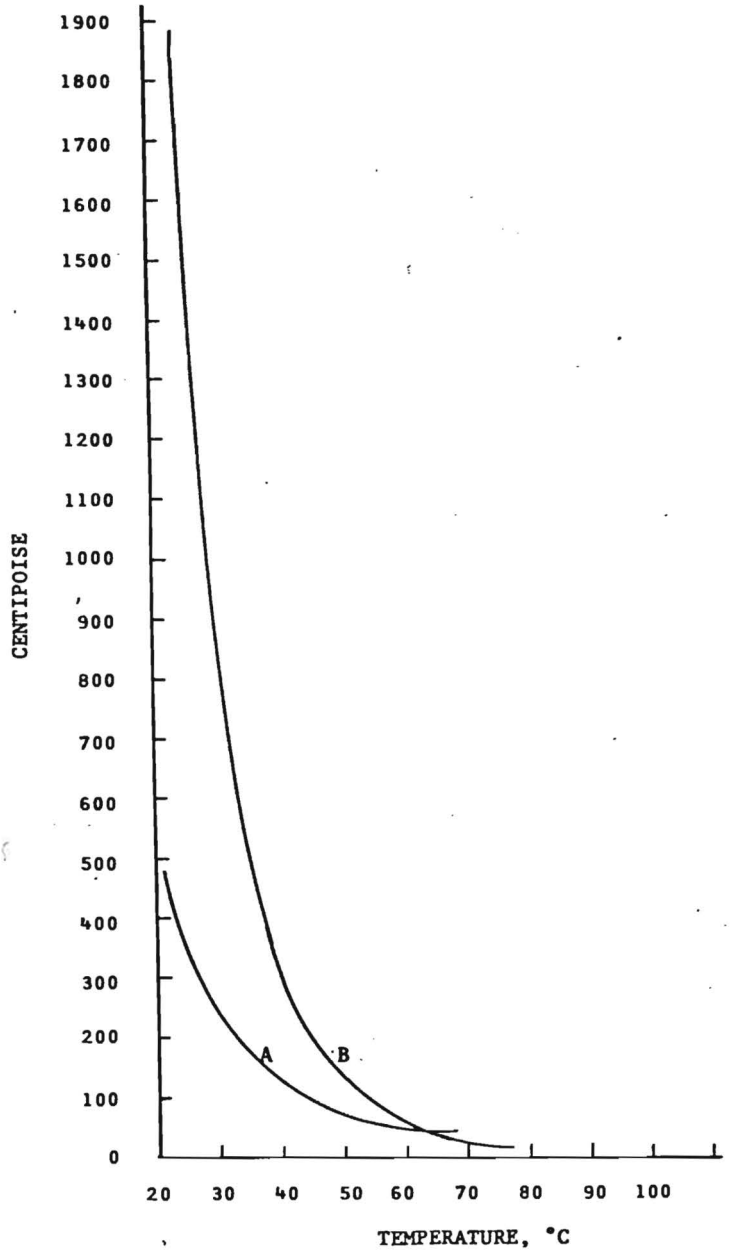

FIGURE 3. Vacuum stripped condenser oil: (A) Initial viscosity curve, and (B) vacuum stripped viscosity curve.

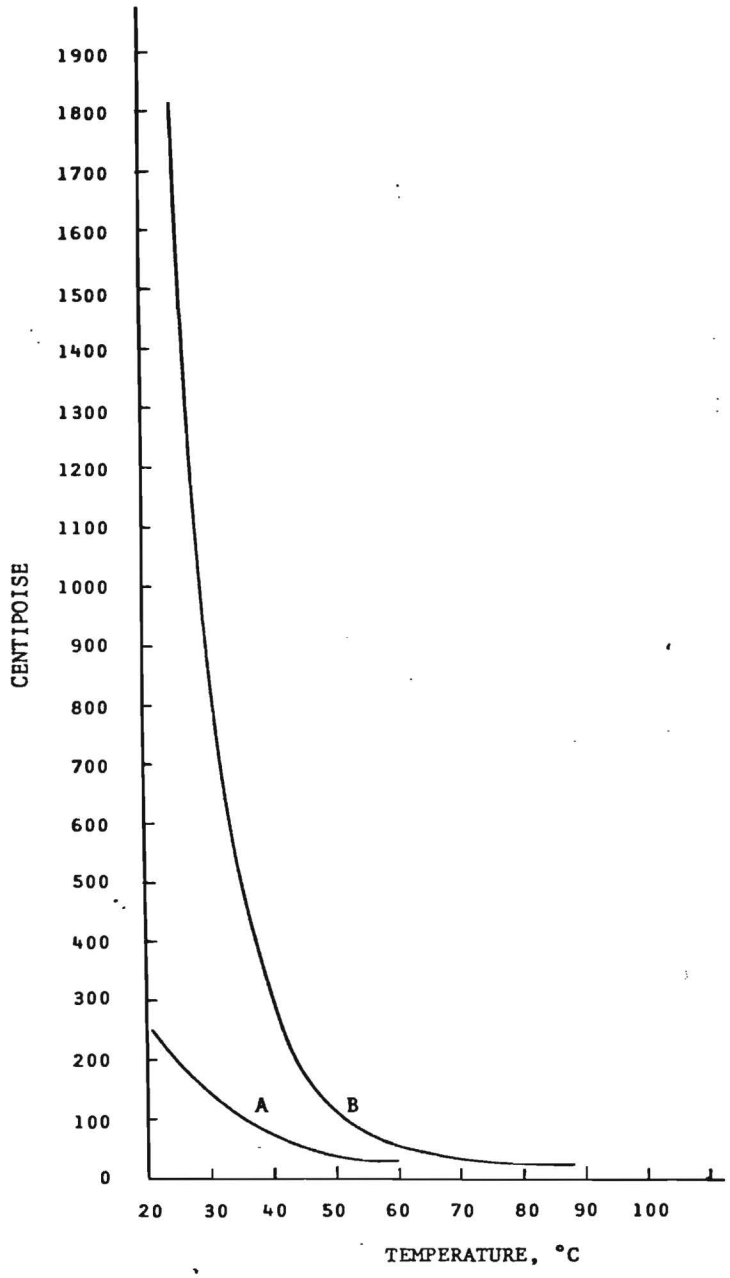

FIGURE 4. Vacuum stripped draft fan oil: (A) Initial viscosity curve, and (B) vacuum stripped viscosity curve.

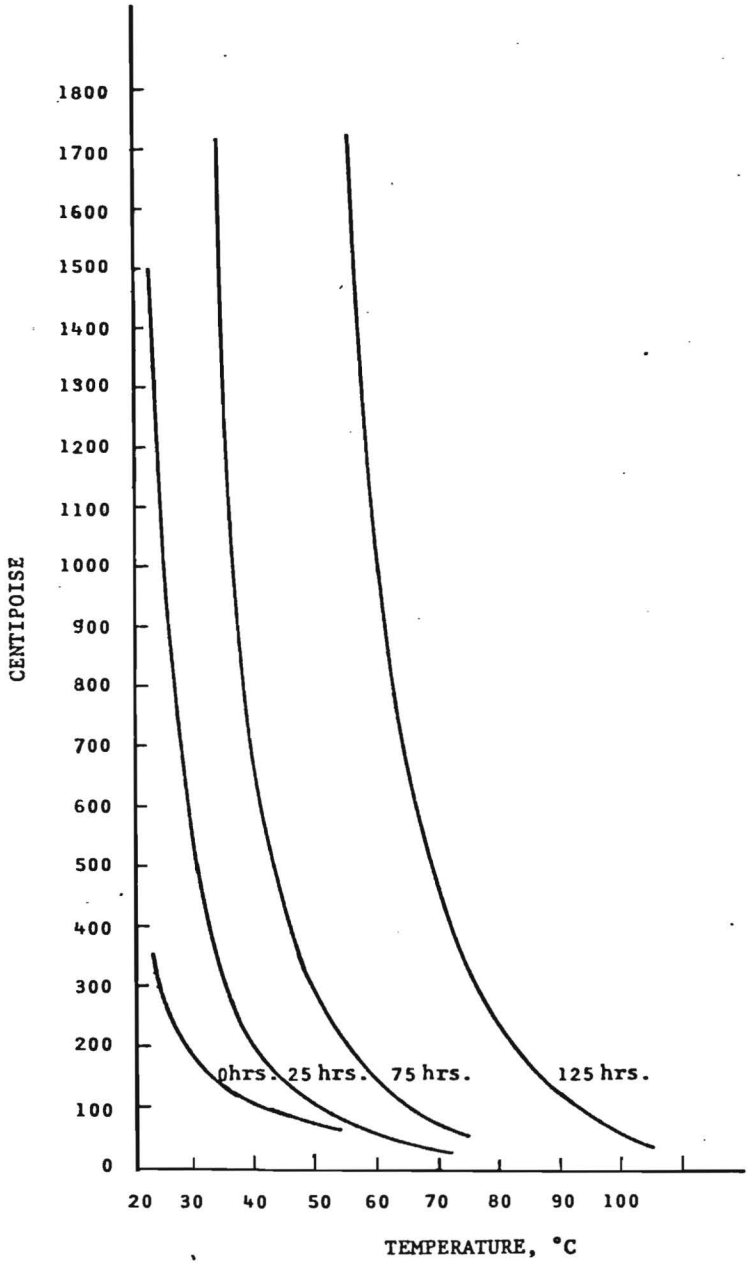

FIGURE 5. Effect of heating condenser oil at 110°C for different time periods on viscosity.

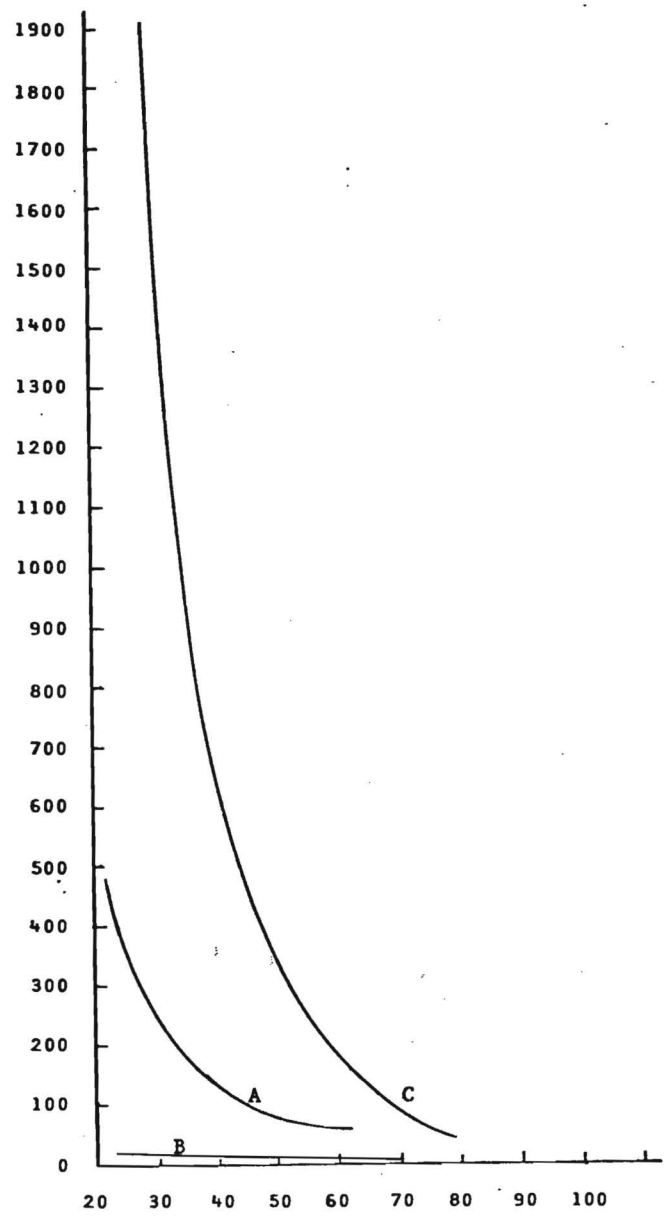

FIGURE 6. Viscosity curves for condenser oil (initial) and #2 and #6 fuel oils: (A) Condenser oil; (B) #2 fuel oil; and (C) #6 fuel oil.

IV. DISTILLATION

Distillation offers a possible method for processing wood oil to produce more desirable and useful products. Therefore, samples of the condenser wood oil were distilled under a variety of conditions.

A. Distillation at Atmospheric Pressure

A sample of condenser oil was distilled at atmospheric pressure, and three distillate phases were obtained--an aqueous phase, a heavy oil phase and a light oil phase. Most of the aqueous phase was obtained at 95°-125°C. Between 125°-190°C, the distillate was mostly heavy oil with some water and light oil. Between 190°-230°C, the distillate was mainly light oil. After approximately 68% of the sample had been collected as distillates, the head temperature began to drop, and the distillation was discontinued. The distillation data are presented in Table V.

TABLE V. Atmospheric Distillation Data

Fraction	*Head Temperature, °C*	*Yield, %*
Aqueous phase[a]	*95°-125°*	*20.7*
Heavy oil	*105°-190°*	*28.4*
Light oil	*190°-230°*	*19.1*
Residue[b]		*25.0*
Total		*93.2*

a. Contained 6.2% organic material as determined by gas chromatography.

b. The residue solidified on cooling to room temperature.

The analytical data on the oil phases and the residue are presented in Table VI.

TABLE VI. Analytical Data--Atmospheric Distillation Fractions

Property	*Light oil*	*Heavy oil*	*Residue*
Density, g/ml	*0.9988*	*1.0423*	-
pH	*3.5*	*2.9*	-
Acid No., mg KOH/g	*52*	*17.8*	-
Elemental analysis			
Carbon %	*67.4*	*74.0*	*60.1*
Hydrogen %	*7.5*	*8.2*	*2.9*
Nitrogen %	*0.1*	*0.7*	*0.8*

B. Vacuum Distillation

A sample of condenser oil was distilled in a simple vacuum distillation apparatus at 0.2-0.4 mm Hg pressure with dry ice and liquid nitrogen traps for recovery of volatile material. The aqueous phase containing light organics was obtained before the head temperature reached 43°C. At 190°C head temperature, the distillation was discontinued as the material in the flask was becoming more viscous and appeared to be approaching a decomposition stage. The vacuum distillation data are presented in Table VII.

The oil fractions 1-4 were combined to obtain a sample of oil for fractionation under vacuum with a spinning band column. Analytical data on the combined oil fractions is given in Table VIII.

TABLE VII. Vacuum Distillation Data

Fraction	Head temperature, °C	Yield, %
Aqueous and light organics phase[a]	Ambient to 43°	23.1
1	43°-125°	17.6
2	125°-140°	2.1
3	140°-180°	18.5
4	180°-190°	2.6
Residue	-	32.4
Total		96.3

a. Contained 46% organic material as determined by G.C. gas chromatography

TABLE VIII. Analytical Data-Vacuum Distillation

Property	Combined fractions 1-4
Density, g/ml	1.091
pH	2.8
Acid No., mg KOH/g	59.6
Heating value, cal/g, Btu/lb	10,964
Elemental analysis	
Carbon, %	62.7
Hydrogen, %	7.7
Nitrogen, %	0.3

C. Vacuum Spinning Band Distillation

A sample of the combined oil fractions from the vacuum distillation (B above) was distilled in a Nester-Faust spinning band distillation column at 0.2-0.4 mm pressure with liquid nitrogen traps for recovery of volatile material. The distillation data are given in Table IX.

TABLE IX. Spinning Band Distillation Data

Fraction	*Head temperature, °C*	*Yield, %*
1	*35-48*	*8.0*
2	*48-58*	*14.6*
3	*58-60*	*8.5*
4	*60-68*	*2.1*
5	*68-74*	*6.9*
6	*74-82*	*6.0*
7	*82-88*	*4.6*
8	*88-98*	*2.8*
9	*98-105*	*5.5*
Flask residue	-	*30.0*
Trap material	-	*7.8*
Total		*96.8*

At a head temperature of 105°C, the distillation had slowed down considerably. The material in the flask was becoming more viscous. The distillation was discontinued. Upon cooling to ambient temperature, the residue in the flask was a very viscous, black tarry material. Additional data on some of the fractions are presented in Section V.

D. Steam Distillation

A sample of condenser oil, 1238 g (14.0% water), was steam distilled. An oily layer, 8.8 g, along with an aqueous layer of 385 g was collected using steam only at a temperature up to 105°C. At this point heat was applied to the flask in addition to steam injection. The distillation was continued up to 190°C. The data on the distillates and flask residue are given in Table X.

TABLE X. Steam Distillation Data

	Temperature		
Material	*Up to 105°C*	*105°-150°C*	*150°-190°C*
Aqueous phase	*385 g*	*420 g*	*279 g*
Water	*354 g*	*359 g*	*228 g*
Organic	*31 g*	*61 g*	*51 g*
Organic phase	*8.8 g*	*33.8 g*	*183 g*
Residue, organic	-	-	*468 g*

Of the original charge, 18.2% distilled as a separate organic phase, and 11.6% organic material was detected by gas chromatography in the aqueous layers. A recovery of only 78.6% was obtained, which indicates that perhaps more organic material was present in the aqueous distillates than was detected.

E. Vacuum Stripping of Water from Wood Oil

The condenser and draft fan wood oils obtained from the Tech-Air facility contained water which does not separate on standing. Samples of the oils without the water were needed for characterization., Vacuum stripping was found to be the most effective means of removing this water. Two experiments for removal of the water were carried out at 0.3 mm of mercury. Dry

ice-acetone and liquid nitrogen traps were used to recover any water and volatile organics. In the first experiment, the flask was heated to 55°C to insure that the water would be removed. Based on the amount of volatile organics recovered, a second experiment was carried out in which the flask temperature was maintained at 25°C. The data are presented in Table XI.

TABLE XI. Vacuum Stripping of Water from Condenser Wood Oil

	Weight	
Phase	Experiment 1 Heated to 55°C	Experiment 2 25°C
Aqueous phase		
Water	12.1	12.9
Organic	4.4	0.0
Organic phase	0.35	1.3
"Dried" oil	82.4	84.3
Total	99.25	98.5

V. LIQUID CHROMATOGRAPHY

Liquid chromatography (L.C.) was selected as one analytical technique which could be used for characterization of wood oils and fractions obtained from them. L.C. appeared to be particularly suitable for these oils since L.C. is carried out at ambient temperature, is capable of high resolution of complex mixtures, and detection of components is nondestructive. The main initial objective of utilizing L.C. in our work with wood oils obtained by pyrolysis is to use a method for "fingerprinting" the raw oils and fractions obtained from them for comparison and

correlation. From preliminary experimental work, the conditions for obtaining survey L.C. chromatograms are as follows: Partisil ODS 5μ column; water-acetonitrile solvent system with 10 to 100% acetonitrile solvent gradient; and the uv detector set at 254 nm.

Representative chromatograms of raw condenser and draft fan oils are given in Fig. 7 and 8, respectively; of the distillate from simple vacuum distillation of condenser oil, Fig. 9; of fractions 1, 5, and 9 from the vacuum distillation of the oil distillate from the simple distillation of condenser oil, Figs. 10, 11, and 12, respectively; of vacuum stripped condenser oil, Fig. 13; and of organic and aqueous phases from steam distillation of condenser oil, Figs. 14 and 15.

VI. RESULTS AND DISCUSSION

The wood oils for this study were obtained from the demonstration facility of the Tech-Air Corporation. The feed material was a mixture of pine bark-sawdust in a ratio of approximately 70:30. The pyrolytic converter is a vertical shaft type reactor in which the feed material is fed in at the top giving a vertical, porous bed of the feed material. Char is removed at the bottom and the gaseous phase passes up through the porous bed of feed material into the off-gas system. The air cooled condenser is operated to condense an organic phase which contains 15% or less water. A second organic phase is obtained from the draft fan located between the condenser and the after-burner for the non-condensed gases.

The condenser and draft fan wood oils obtained for this study were free flowing liquids and had a dark brownish color and a burnt odor. The water in the oil is well dispersed or emulsified and does not separate into an aqueous phase on standing. The densities of the oils are greater than water. The oils are acidic and exhibit some corrosive properties. The heating

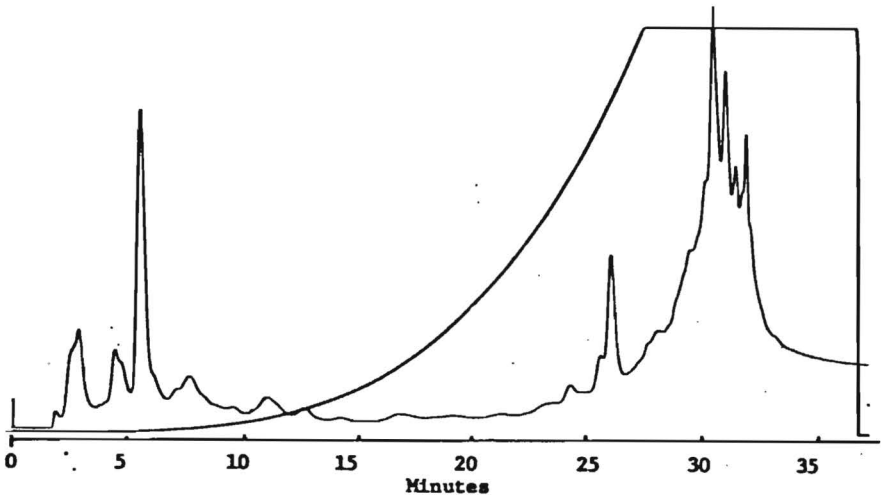

FIGURE 7. Survey liquid chromatogram of raw condenser oil.

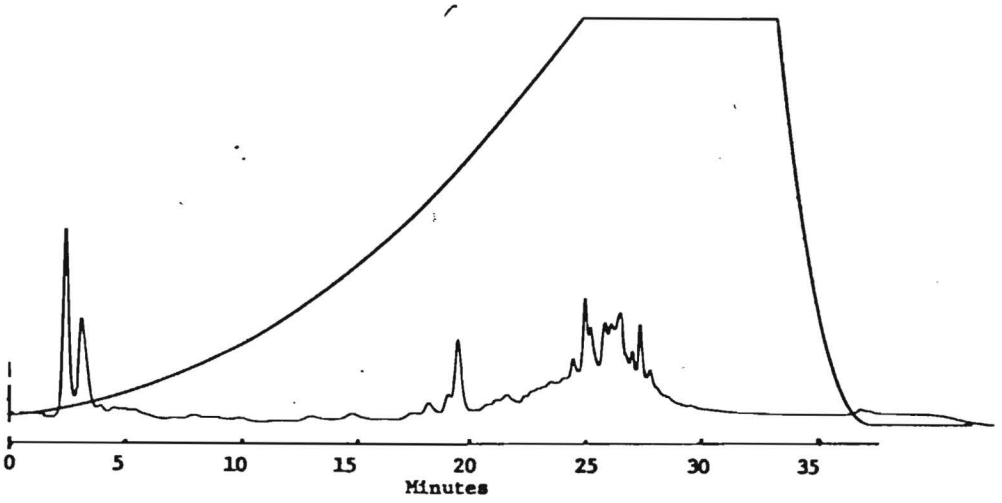

FIGURE 8. Survey liquid chromatogram of draft fan oil.

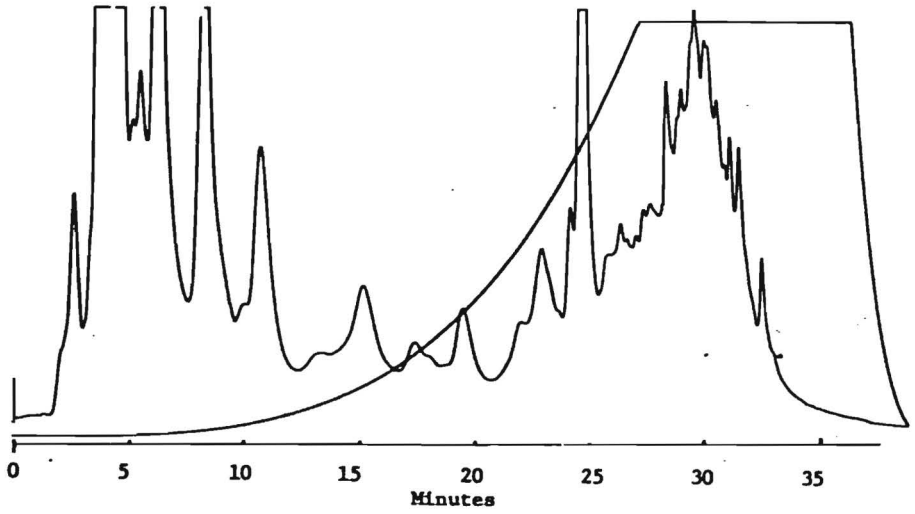

FIGURE 9. Survey liquid chromatogram of combined fractions from vacuum distillation.

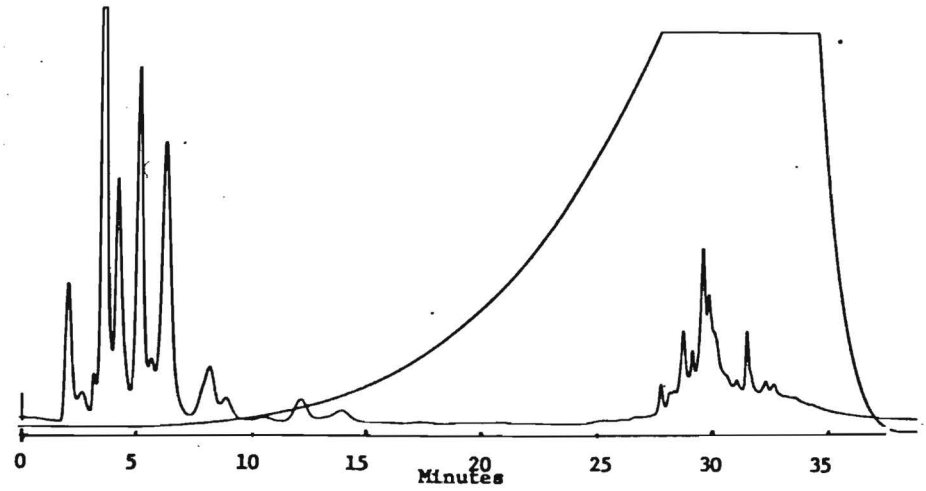

FIGURE 10. Survey liquid chromatogram of spinning band 1 fraction.

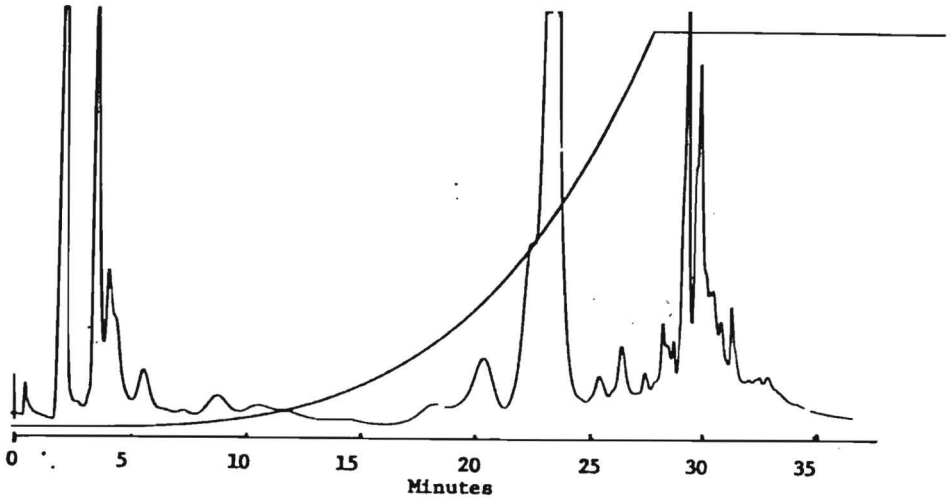

FIGURE 11. Survey liquid chromatogram of spinning band 5 fraction.

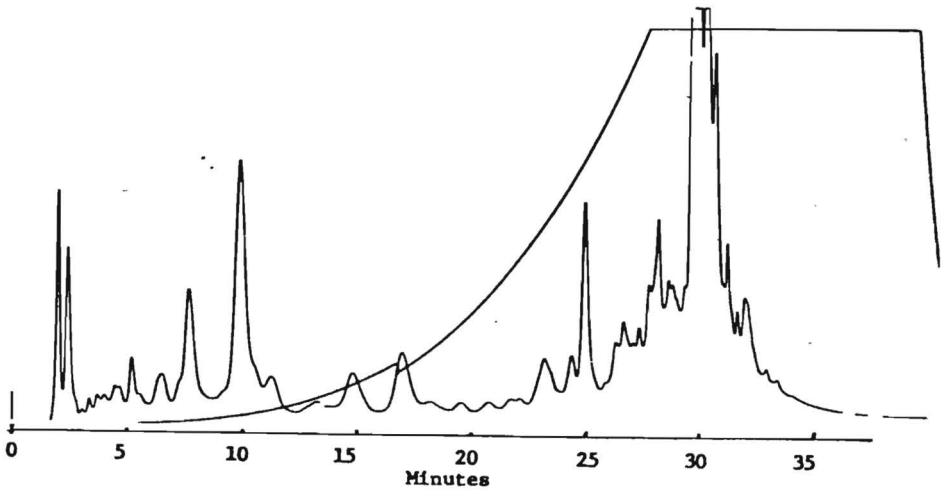

FIGURE 12. Survey liquid chromatogram of spinning band 9 fraction.

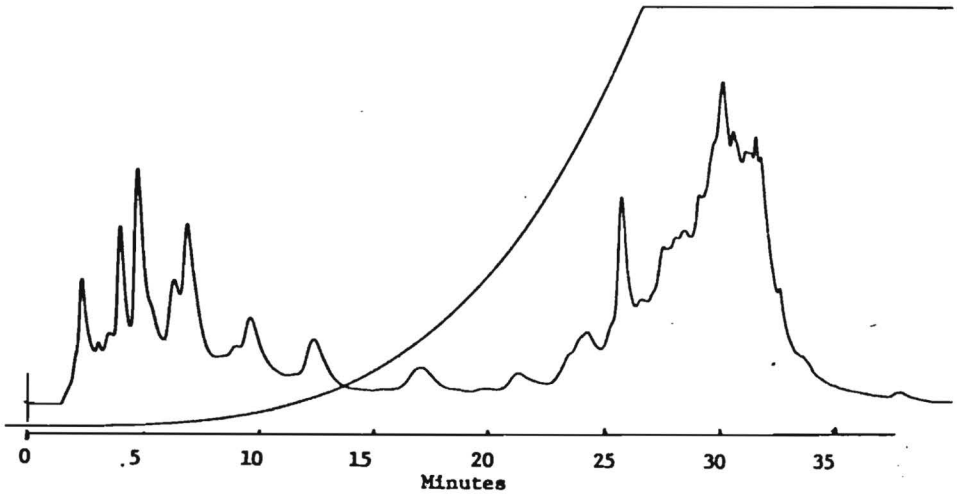

FIGURE 13. Survey liquid chromatogram of condenser oil vacuum stripped without heat.

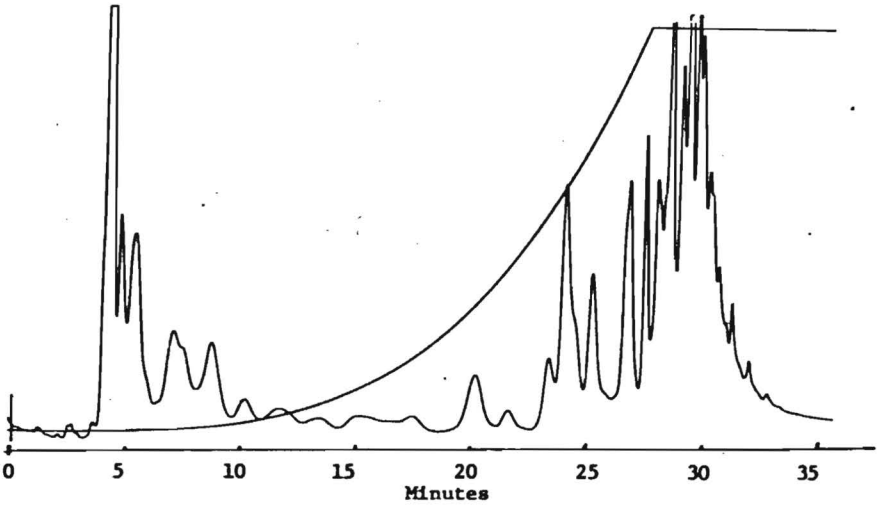

FIGURE 14. Survey liquid chromatogram of 100°-105°C organic layer from steam distillation.

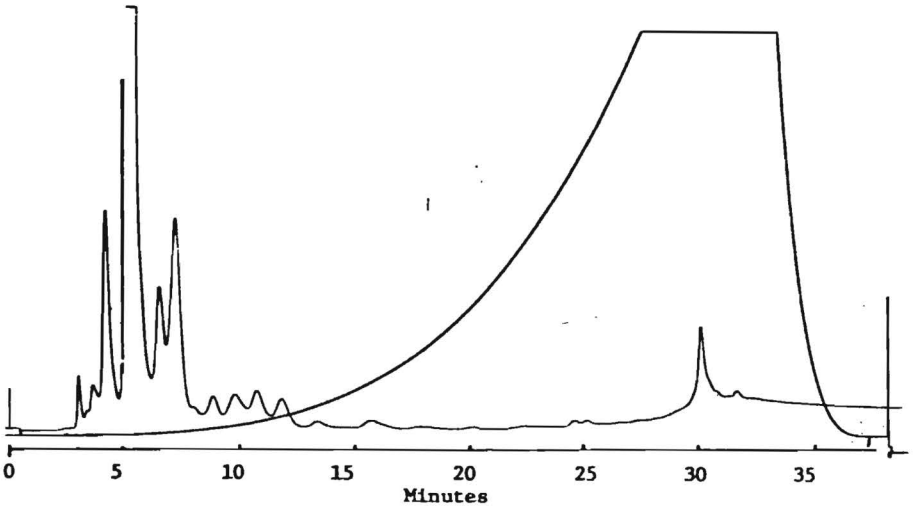

FIGURE 15. Survey liquid chromatogram of 100°-105°C aqueous phase from steam distillation.

values of the oils are less than those of fuel oils, since the wood oils contain a fair percentage of oxygen. The properties of samples of the condenser and draft fan oils which were stored for eight months showed some changes (Table III). However, these changes do not appear to be highly significant in the utilization of the oils as fuels.

The wood oils have greater densities than the #2 and #6 fuel oils. For this reason the heating values of the wood oils are a greater percentage of the heating values of the fuel oils when compared on a volume basis than when compared on a weight basis. The very low sulfur content of these wood oils and similar oils obtained from different lignocellulosic materials is very significant. One utilization approach is blending or co-firing of these oils with sulfur containing fuels to reducing sulfur emissions at a given plant to acceptable levels.

The viscosity of oils is an important property in the handling of these materials. The viscosities of a number of wood oil samples and #2 and #6 fuel oils were determined and are given in Figs. 1 through 6. The viscosities of the wood oils changed some on storage at 0°C and ambient temperature over an eight month period. These changes should not have any great effect on the handling characteristics of the oils. The vacuum stripped oils had much higher viscosities at the lower temperatures, but approached the viscosities of the fresh oils at the higher temperatures. These results are essentially what would be expected since the vacuum stripping removes the water in the oils. Sealed samples of the condenser oil were heated at 110°C for different time periods, and the viscosity curves are given in Fig. 5. The curves show that the viscosity of the heated samples increases markedly with time. The curve for the sample heated 75 hours is very similar to the viscosity curve for #6 fuel oil. These data show that prolonged heating of oils obtained by pyrolysis must be considered in the materials handling of the oils.

A number of distillation experiments were carried out with the condenser wood oil. The data from these initial experiments indicate that distillation is a potential processing method for obtaining fractions which could have greater utility and value than as a fuel. Additional study is needed on the chemical characteristics of the distillates, however, to find specific uses for them. The wood oils are heat sensitive, and in both atmospheric and vacuum distillation at heat temperatures of 190°-200°C, the material in the flask becomes more viscous and decomposes if heating is continued. The distillate oil from vacuum distillation of condenser oil exhibits the same behavior as a sample fractionated in a spinning band column at 0.2-0.4 mm pressure.

Liquid chromatography is an excellent analytical tool for characterization of oils produced by pyrolysis of lignocellulosic materials. Chromatograms on the condenser and draft fan oils and different distillate oils obtained by different distillation techniques show that the oils contain a large number of components. An examination of Figs. 10, 11, and 12 for three different fractions of oil obtained from the vacuum fractionation of condenser distillate oil shows that each of these fractions contains a large number of components.

VII. SUMMARY

The condenser and draft for oils produced by pyrolysis of a pine bark-sawdust mixture has been characterized and tested by a variety of methods. The oils, as produced, contain approximately 15% or less water, which is well dispersed. The heat values of the oils vary from about 60 to 70% of the heating values of fuel oils on a volume basis. The oils contain essentially no sulfur, and therefore do not create any sulfur emission problems when burned as a fuel. The tests for oil samples stored eight months at 0°C and ambient temperature indicate that no significant changes occurred which would affect the use of the oil as a fuel. The oils are acidic and exhibit some corrosive properties. The viscosity of the oils increased with prolonged heating at 110°C, and this factor would have to be considered in the handling of the oil. Also, the oils start to degrade and decompose when heated to approximately 200°C. The oils contain a fair percentage of oxygen mixtures with a large number of components as shown by liquid chromatographic analysis. It is reasonable to assume that many of the components are oxygen containing compounds.

REFERENCES

1. "Conference on Silviculture Plantations," The Mitre Corporation/Metrek Division and Georgia-Pacific Corporation, Reston, Va., February 15-16, 1977.
2. J. A. Knight, M. D. Bowen, and K. R. Purdy, "Pyrolysis--A Method for Conversion of Forestry Wastes to Useful Fuels," Presented at poster session, Conference-Energy and Wood Products Industry, Forest Products Research Society, Atlanta, Ga., November 15-17, 1976.

APPENDIX B

EXPENDITURES

June 21, 1976-January 31, 1978

APPENDIX B

EXPENDITURES

The expenditures from the initiation of the project through January 31, 1978, were as follows:

(a)	Direct wages and salaries	$ 53,322.80
	Retirement (9.35% of applicable wages and salaries)	4,590.84
	Travel	767.30
	Material and Supplies	5,321.47
	Material and Supplies (Encumbered)	476.25
	Capital	922.07
	Overhead (68% of direct wages and salaries)	36,259.51
	Total	$ 101,660.24
(b)	Total Budget	$ 130,000.00
	Expenditures through September 30, 1977	101,660.24
	Remaining Funds	$ 28,339.76

B-469

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

Atlanta, Georgia

Progress Report No. 6

February 1, 1978--May 31, 1978

Project B-469

UTILIZATION AND/OR STABILIZATION OF PYROLYTIC OIL FROM PYROLYSIS OF AGRICULTURAL, MUNICIPAL AND OTHER WASTES

by

J. A. Knight

Grant No. R 804 416 010

Performed for

Municipal Environmental Research Laboratory

Environmental Protection Agency

Cincinnati, Ohio 45268

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SECTION 1

SUMMARY

The major emphasis and effort during this report period has been directed toward the development of separation technology for pyrolysis oils that will yield fractions of oils which will have greater utility as chemical materials and/or feedstocks. Five major approaches involving extraction techniques were tested at the bench level on a batch basis. These approaches are:

A - Extraction of oil sequentially with water at 25°C, 50°C and 95°C.

B - Extraction of oil sodium sulfate solution (salting out effect).

C - Extraction of oil simultaneously with an organic solvent and water (three phase system).

D - Extraction of sodium hydroxide solution at different pH ranges with methylene chloride.

E - Extraction of organic solvent solutions of pyrolysis oil with water.

The pyrolysis oil, after removal of the volatile organics and water by vacuum stripping, contains three broad classes of organic substances--phenolics, approximately 20-25%; aromatic neutral compounds, such as ethers and ketones, 40-48%; and a group of substances which have "sugar-like" characteristics, approximately 23-27%. Hence, it would be very desirable to separate the pyrolysis oil into a fraction of mainly phenolics, another fraction of mainly aromatic neutral compounds and a third fraction of mainly "sugar-like" substances. In general, in the process approaches tried at the bench scale, an aqueous fraction was obtained which contained approximately 50% of the phenolics and most of the "sugar-like" substances. The aqueous insoluble fraction contained the remainder of the phenolics (~ 50%) along with most of the aromatic neutral compounds. Separation of aqueous fraction and the water insoluble fraction into their major chemical classes would yield a total of four fractions--

1 - a water soluble phenolic fraction;

2 - a water insoluble phenolic fraction;

3 - a fraction containing mainly the "sugar-like" substances; and

4 - a fraction containing mainly aromatic neutral compounds.

A possible method for separation of the aqueous phase into the phenolics and the "sugar-like" substances is the salting out technique as used in process B.

Fractional distillation and alkaline extraction of the aqueous insoluble fraction are possible techniques for separating this fraction into the phenolics and aromatic neutral compounds. These four fractions should find extensive applications in areas such as resins, rubber and asphalt industries, solvents and starting materials for chemical processing.

SECTION 2

DISCUSSION

Chemical Classes of Compounds in Pyrolysis Oil

Separation of raw pyrolysis oil into fractions, each of which contain a high concentration of a chemical class of compounds, is the initial major step in the utilization of pyrolysis oil as a chemical feedstock and in increasing its monetary value. The broad classes of chemical substances in raw pyrolysis oil are phenolics, approximately 17-22%; aromatic neutral compounds, such as aromatic ethers and ketones, approximately 34-42%; acids (mostly aliphatic), approximately 6-7%; and a group of substances which have "sugar-like" characteristics, approximately 20-24%. In addition, pyrolysis oil produced by the Georgia Tech pyrolysis process has approximately 8-13% water which is well emulsified and does not separate on standing.

Potential Applications for Fractions of Pyrolysis Oil

The phenolic group represents a class of compounds that should find immediate utilization and application in the resin industry, i.e. in the preparation of phenol-formaldehyde resins. Resins of this type find widespread utility in the plywood and particle board industry. The aromatic ethers and ketones represent very interesting groups of compounds which must be synthesized from simpler organic compounds. The availability of these aromatic compounds from pyrolysis oils could lead to new and useful applications. Some of the aromatic ethers are used as starting material in the preparation of resins. In general, the aromatic ethers and ketones should be excellent candidates as potential solvents, plasticizers, and starting materials for chemical processing.

Objective of Separation Technology

The objective of our separation work with pyrolysis oils therefore is to develop methods that would produce initially two major fractions, one which contains predominately phenolic compounds and another fraction which would contain predominately the aromatic neutral compounds. In order to accomplish this goal, the processing technology is focused on the separation

of the water, acids and the "sugar-like" substances. The "sugar-like" substances have chemical characteristics based on our analytical work similar to carbohydrates and sugars. It appears to be highly desirable to remove these substances as a separate fraction because of the nonaromatic character and potential deleterious effects, if present, in the fractions containing phenolics and a mixture of aromatic ethers and ketones, on the utilization of these fractions. Therefore, the focus of the separation experimental work has been on developing separation technology which would yield the desired phenolic fraction and the aromatic ether and ketonic fraction.

Separation Technology Approaches

Important factors that must be considered in developing separation technology for pyrolysis oils are processing steps which are relatively simple and the economics of the process. To date, the laboratory work has been at the bench scale with batch processing. The separation techniques and results are presented in the experimental section. Based on our experimental results with both raw oil and vacuum stripped oil, the first step in the processing of pyrolysis oil would be to remove the volatiles and the major portion of the water at reduced pressure and ambient temperature. It has been our experience that the vacuum stripped oil gives better results than the raw oil. In addition, the volatile acids are removed in this step along with the water. Since the major acidic component is acetic acid, the recovery of acetic acid from this aqueous fraction is technically feasible.

Five major approaches involving extraction techniques were tested at the bench level on a batch basis. These approaches, which are discussed in the experimental section, are as follows:

A - Extraction of oil sequentially with water at 25°C, 50°C and 95°C.

B - Extraction of oil with sodium sulfate solution (salting out effect).

C - Extraction of oil simultaneously with an organic solvent and water (three phase system).

D - Extraction of sodium hydroxide solution at different pH ranges with methylene chloride.

E - Extraction of organic solvent solutions of pyrolysis oil with water.

Each of these approaches offer possibilities that can be utilized in a final process that will achieve the objective of this investigation. The significant results for each approach will be presented with pertinent comments.

From process A, approximately 50% of the original raw oil was isolated as a water insoluble organic fraction, which contained about 20% phenolics and 80% aromatic neutrals. The separation of this fraction into the two major compound classes is very desirable. Processing techniques that are potentially useful are fractional distillation and other extraction steps. The three aqueous fractions, if combined, would contain approximately 34% of the original oil with 27% phenolics and 73% "sugar-like" substances. A good potential means for separation of these two chemical classes is the use of the salting-out technique which is the basis of process B. The advantage of process A is that water is a cheap solvent and nonhazardous, and the process should be relatively simple.

Process B, which involves essentially a salting out effect with sodium sulfate, offers an excellent possibility for separation of the "sugar-like" substances. The first step would be as depicted in Figure 3. The aqueous fraction contains organics with approximately 70% phenolics. This separation could possibly be improved by determining optimum conditions. The insoluble fraction could be extracted with water to remove the "sugar-like" substances leaving an insoluble oil fraction. Therefore, the results with these two process approaches indicate that incorporating the salting-out effect into the separation process offers a potential for isolating the major portion of the "sugar-like" substances as a separate fraction. The best of the two approaches needs to be determined experimentally, i.e. use the salting-out effect initially as depicted in Figure 3 or use it on the combined aqueous fractions which are produced in process A as presented in Figure 2.

Process C, the three phase system, offers some interesting separation possibilities. It should be noted that the phenolics in the oil are separated about 50-50 in processes A and B and in process C, the aqueous phase contains about 50% of the phenolics and the remaining 50% is about evenly divided between the ether phase and the insoluble oil phase. Based on our analysis for the three phase separation, the phenolics in the aqueous phase are mainly dihydroxy phenolics, those in the ether phase are alkyl phenols and those in the insoluble oil phase are ether phenols. Based on these data, some degree of fractionation of the phenolic substances has been achieved. The aqueous fraction could be subjected to the "salting-out" technique to provide separation of the phenolics from the "sugar-like" substances. Separate fractional

distillation of the oil and ether fractions should yield fractions with high concentration of phenolics and the aromatic neutrals.

The three phase approach with anisole produced results as shown in Figure 5. The quantities of the components in the aqueous fraction are about the same as when diisopropyl ether was used. The anisole, however, dissolves a much greater portion of the oil than diisopropyl ether. The diisopropyl ether is the solvent of choice based on available data extraction in a three phase system.

In process D, two percent sodium hydroxide solution was used as a solvent for the oil followed by extraction with methylene chloride at three different pH ranges, 8 to 10, 5 to 7, and 1 to 3. Approximately, 53% of the oil charge dissolved in 300 ml of 2% NaOH. The extraction with CH_2Cl_2 at pH 8 to 10 gave predominantly aromatic neutrals whereas at the low pH range, the extract contained predominantly phenolics. Approximately 55% of the phenolics were in the aqueous phase with the remainder distributed in the three CH_2Cl_2 extracts. The remainder of the charge dissolved in 400 ml of 2% NaOH, and the solution was extracted in the same manner as above. It should be noted that in the first CH_2Cl_2 extract, approximately 92% of the organics was aromatic neutral compounds. Also, in the aqueous phase, approximately 58% of the organics was phenolics. Additional bench scale work is needed with this process to determine its usefulness as a method for processing pyrolysis oil.

Pyrolysis oil is soluble in a number of organic solvents such as methylene chloride, n-butanol and amyl alcohol. Two solutions of pyrolysis oil in methylene chloride were extracted with water followed by extraction of the aqueous solution in one experiment with diisopropyl ether and in the second experiment with methyl isobutyl ketone (MIBK). The results are shown schematically for the two experiments in Figures 7 and 8, respectively. A significant result of these two experiments is that the "sugar-like" substances are concentrated in the aqueous phase along with 50 to 60% of the phenolics in the oil. The methylene chloride fraction contains phenolics and aromatic neutral compounds which could be fractional distilled to provide more desirable and useful fractions of the oil. The aqueous fraction could be treated by the salting out technique to yield a fraction with a much higher concentration of phenolics. Another approach to the treatment of the aqueous

fraction is extraction with MIBK. The extraction of the aqueous fraction with MIBK gave a solution with approximately 92% phenolics, which represents approximately 35% of the phenolics in the aqueous fraction.

A solution of pyrolysis oil in n-butanol was extracted with water to determine the separation that would be obtained and the results are shown schematically in Figure 9. The "sugar-like" substances are distributed between the aqueous fraction and the n-butanol fraction which is not a desirable result. Consequently, this approach was not pursued.

Pertinent Observations about the Separation Technology Approaches

An examination of the data from the process approaches discussed above shows that for each approach approximately 50% of the phenolic content of the oil is in the aqueous fraction with the remainder in the insoluble oil phase or in the organic solvent phase. This could be of significance in that each of these phenolic fractions could have greater utility for specific uses than a single combined fraction of the phenolics. The aqueous fractions from all of the approaches contain relatively large amounts of "sugar-like" substances with the exception of the salting out technique. For the salting out experiment, the ratio of phenolics to the "sugar-like" substances was 2.3 to 1 on a weight base whereas in the others the ratios are in the 1 to 3 range. The salting out technique, therefore, must be seriously considered as an approach for concentrating the phenolics in the aqueous fraction.

The aqueous insoluble fractions contain approximately 50% of the phenolic content of the oil along with most of the aromatic neutral compounds with ratios of phenolics to aromatic neutral compounds in the range of 1 to 3 and 1 to 4. The separation of this fraction into the two major classes of compounds could possibly be accomplished by fractional distillation or extraction with an alkaline solution.

The two process approaches that appear to be most promising are Processes A and C with the use of the salting out technique as described for Process B. More data is needed with these processes in order to design a stepwise continuous process for research and development work with the goal of designing a pilot plant for continuous processing of pyrolysis oil.

The analysis of pyrolysis oils and fractions of the oils produced by separation processes is extremely important in the development of these processes. The pyrolysis oils are complex mixtures of a wide variety of organic compounds and therefore, analysis is a difficult task. In our studies, methods are needed which give data on classes of compounds, such as the phenolics. A nonaqueous titration technique was developed for analyzing the pyrolysis oils for the phenolics and carboxylic acids. It is not a highly precise analytical procedure, but it does provide very useful data on the phenolic content of pyrolysis oils and fractions of the oils. In examination of the data in the experimental section, this should be considered as in some cases material balances may not be as close to 100 percent as one might expect.

SECTION 3

EXPERIMENTAL

SEPARATION TECHNIQUES

Vacuum Stripping of Raw Oil

Based on a number of extraction and separation experiments with raw pyrolysis oils, vacuum stripped oil gives better results than raw oil. The vacuum stripping provides for the removal of the volatile organics and most of the water in the oil with subsequent recovery of these organic compounds. Our analysis show that the major organic component in the volatile fraction is acetic acid. For these reasons, our separation techniques are based on using vacuum stripped oil. Figure 1 shows schematically the vacuum stripping of the oil with yields.

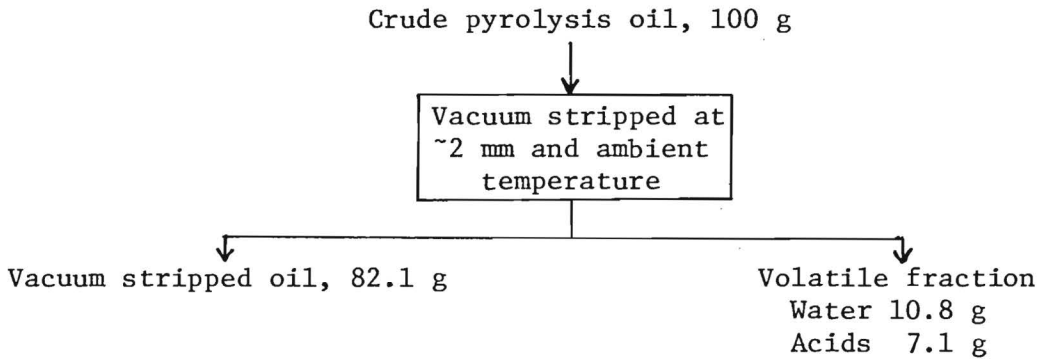
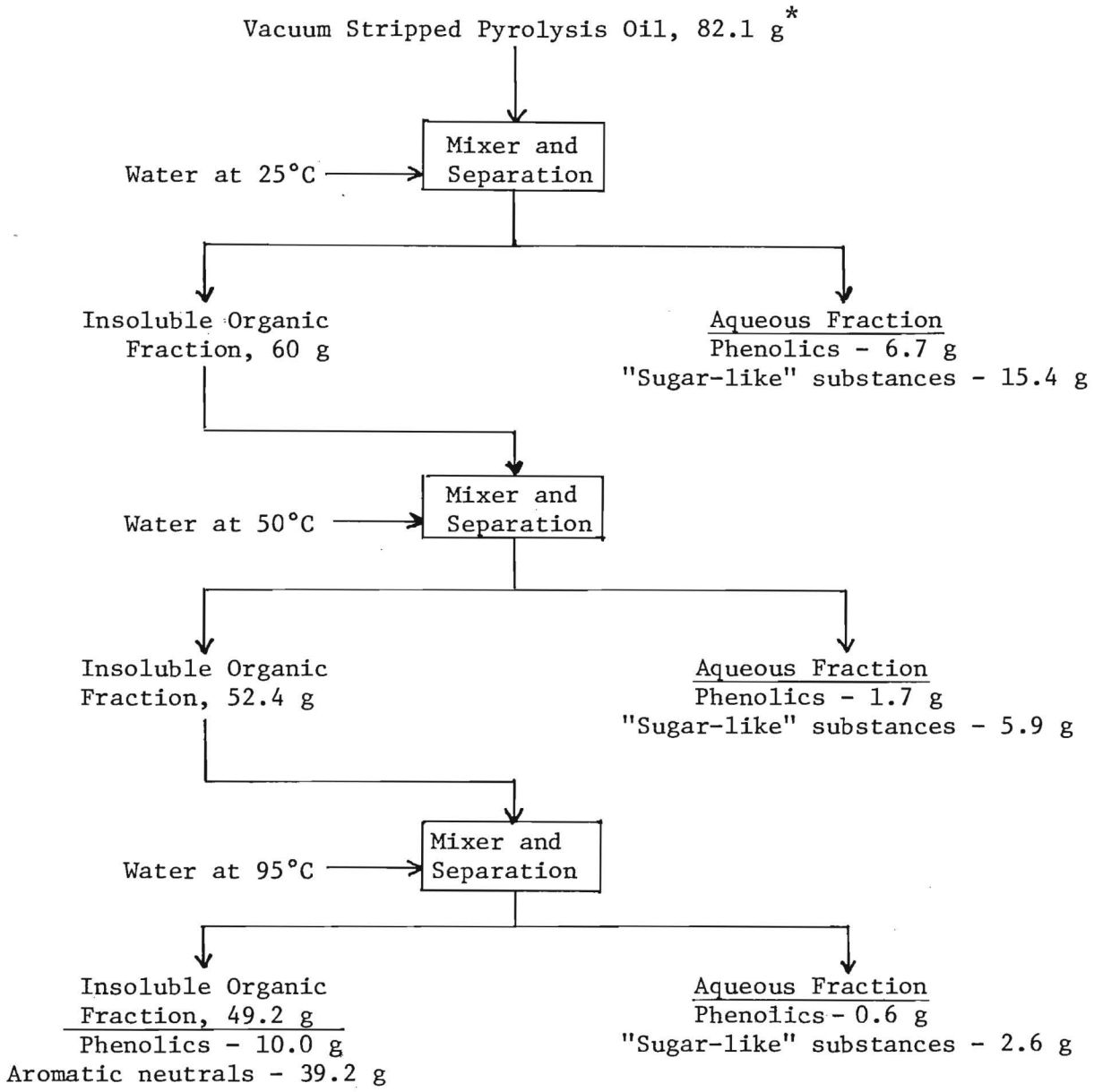


Figure 1. Removal of Volatiles from Pyrolysis Oil

Extraction of Oil Sequentially With Water at 25°C, 50°C, and 95°C

A sample of vacuum stripped oil was extracted sequentially with water at 25°C, 50°C and 95°C in an effort to separate the more water soluble substances. Figure 2 shows schematically this separation process and the recovery of the different material fractions are given in Table 1.

The significance of these results is that the oil can be separated into water soluble and water insoluble fractions which offer the opportunity for recovery of very useful fractions of aromatic compounds. The water insoluble fractions, based on our analysis, is composed of phenolics and neutral



*100 g raw oil will yield 82.1 g of vacuum stripped oil.

Figure 2. Extraction of Oil Sequentially With Water at 25°C, 50°C, and 95°C

Table 1. Yields of Fractions from Water Extraction of Oil

	Water Insoluble Fraction	Water Soluble Fractions			
		25°	50°	95°	Total
Phenolics	10 g	6.7 g	1.7 g	0.6 g	9.0 g
Aromatic neutrals	39.2 g	--	--	--	--
"Sugar-like" components	--	15.4 g	5.9 g	2.6 g	23.9 g
Totals	49.2 g	22.1 g	7.6 g	3.2 g	32.9 g

aromatics. The seapration of this fraction into a highly concentrated phenolic fraction and a highly concentrated fraction of aromatic neutral compounds could probably be accomplished by either fractional distillation or extraction with alkaline solution. The aqueous phases could be combined and subjected to a separation of the components with an aqueous salt solution as described in the section on Extraction of Oil With Sodium Sulfate Solution to yield a fraction with mainly phenolics and another fraction with mainly "sugar-like" substances.

Extraction of Oil with Sodium Sulfate Solution

An extraction experiment with a sodium sulfate solution (90% saturated) was conducted to determine if extraction with aqueous salt solutions would offer a useful separation of the oil. The schematic for this extraction is shown in Figure 3.

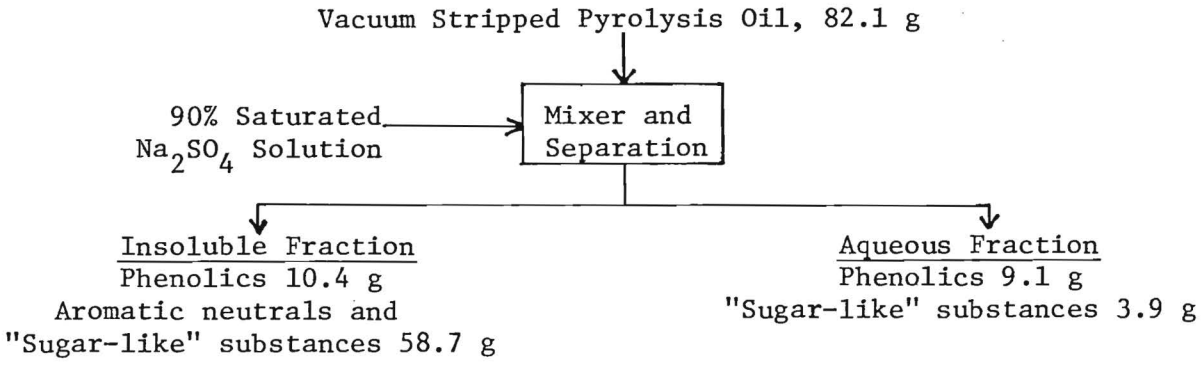


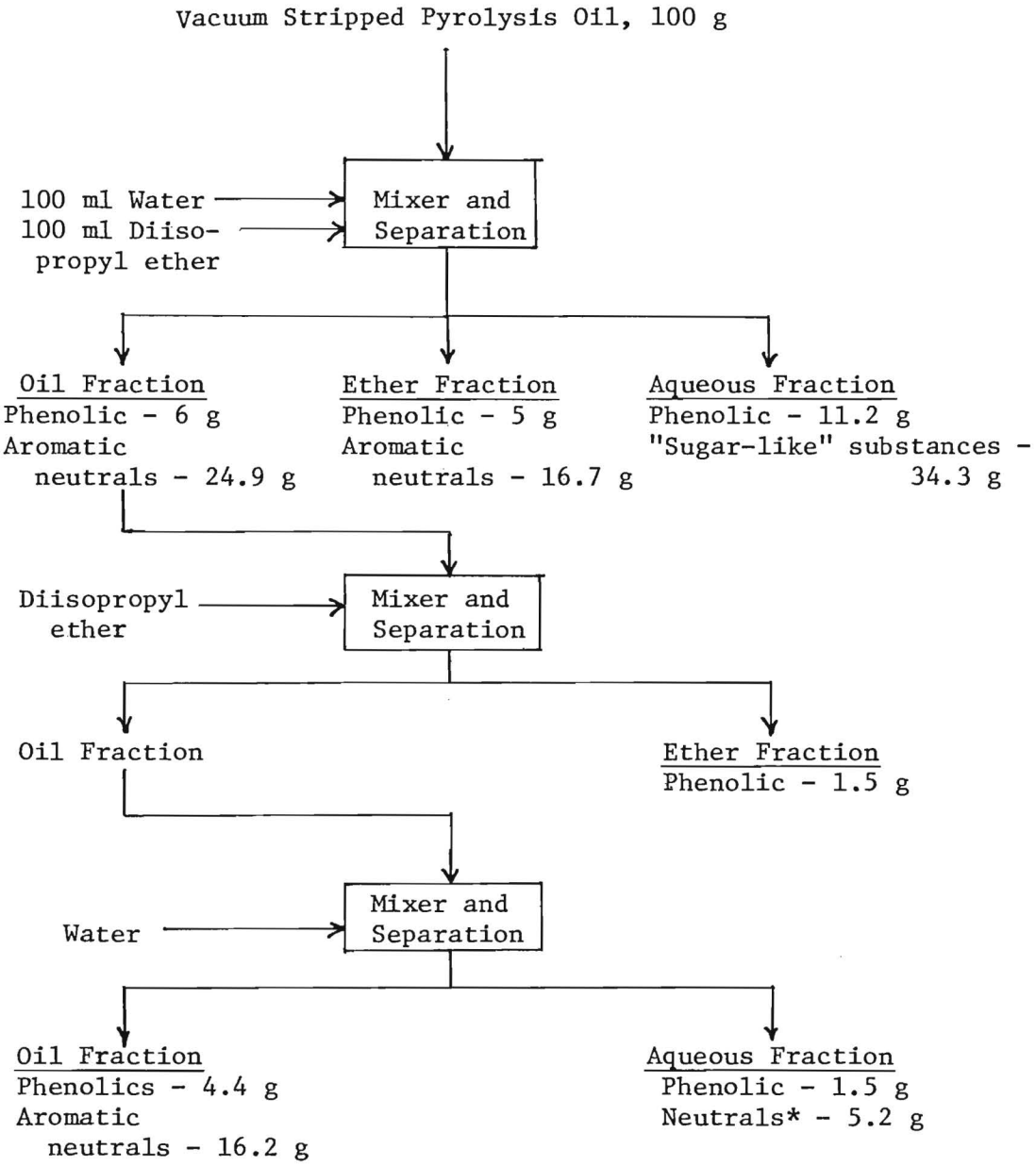
Figure 3. Extraction of Oil with Sodium Sulfate Solution

The importance of these results is that with the sodium sulfate solution approximately 82% of the "sugar-like" substances are in the insoluble fraction with about 18% in the aqueous fraction. The phenolics are approximately 70% of the organics in this aqueous fraction. There are two approaches that can be used involving the sodium sulfate extraction. One approach would be to use the sodium sulfate extraction as the first step as shown in Figure 3 to an aqueous fraction of mainly phenolics. The insoluble organic fraction would then be treated with water extraction as depicted in Figure 2 to remove the "sugar-like" substances. The other approach would be to treat the oil as outlined in Figure 2. The three aqueous fractions would then be combined followed by the addition of sodium sulfate. This approach could possibly provide a good separation between the phenolics and the "sugar-like" substances. The addition of a water insoluble organic solvent may be necessary in such a step to serve as a solvent for the "sugar-like" substances.

Extraction of Oil Simultaneously With Organic Solvents and Water--Three Phase System

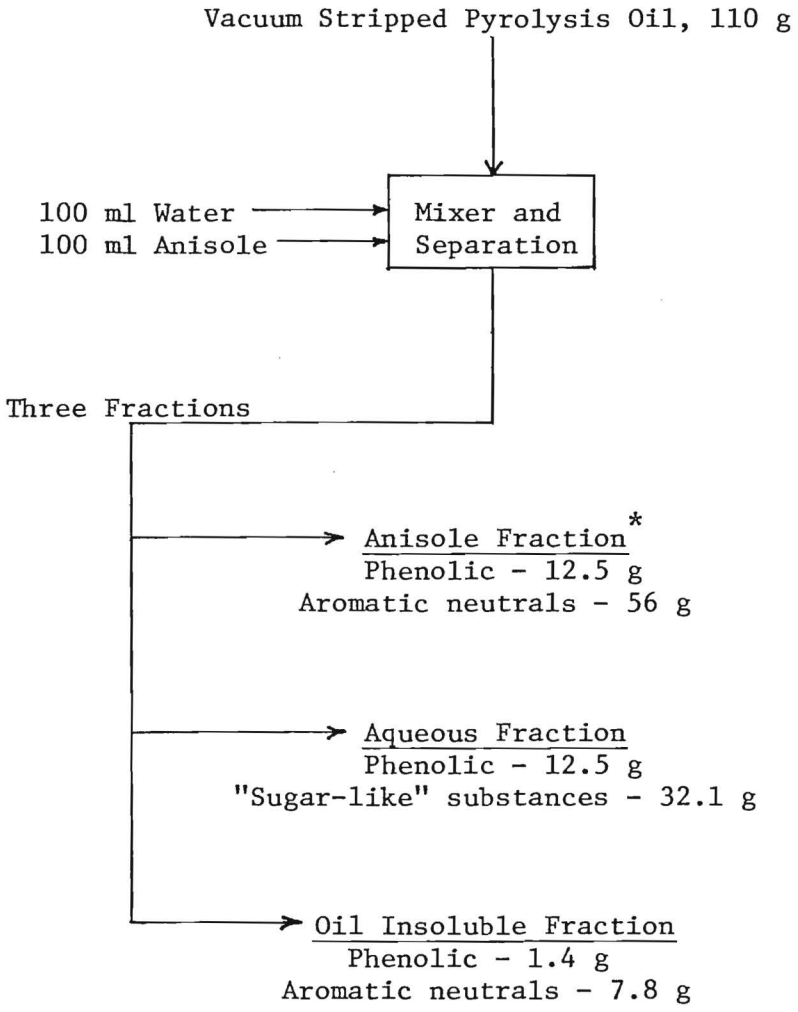
Organic solvents offer a real potential for effecting separation of pyrolysis oils into fractions which contain very similar organic compounds. Some extractions with diisopropyl ether and anisole (methyl phenyl ether) were tired with vacuum stripped oil. It was found difficult to have good contact of the organic solvent with only the oil because the oil became viscous. Addition of an equal volume of water to the mixture produced a nonviscous three phase system containing an ether phase, an aqueous phase and a heavy oil phase. The schematic for diisopropyl ether and water separation along with yields is shown in Figure 4 and the schematic for anisole and water, Figure 5. Based on our analysis, the phenolics in the water fraction are mainly dihydroxy phenols; in the diisopropyl ether phase, alkylphenols; and in oil phase, ether phenols. The aqueous phases from both of the diisopropyl ether-water separations could be combined and possibly separated into a highly concentrated phenolic fraction by salting out the "sugar-like" substances with addition of sodium sulfate or some other salt.

In the anisole experiment, the phenolics were evenly divided between the anisole fraction and the aqueous fraction with a small amount in the oil insoluble fraction. About 88% of the aromatic neutrals were extracted



*Chemical nature unknown.

Figure 4. Combined Diisopropyl and Water Extraction of Pyrolysis Oil



*The removal of all anisole from this fraction was difficult so that total recovery is greater than 100%.

Figure 5. Combined Anisole and Water Extraction of Pyrolysis Oil

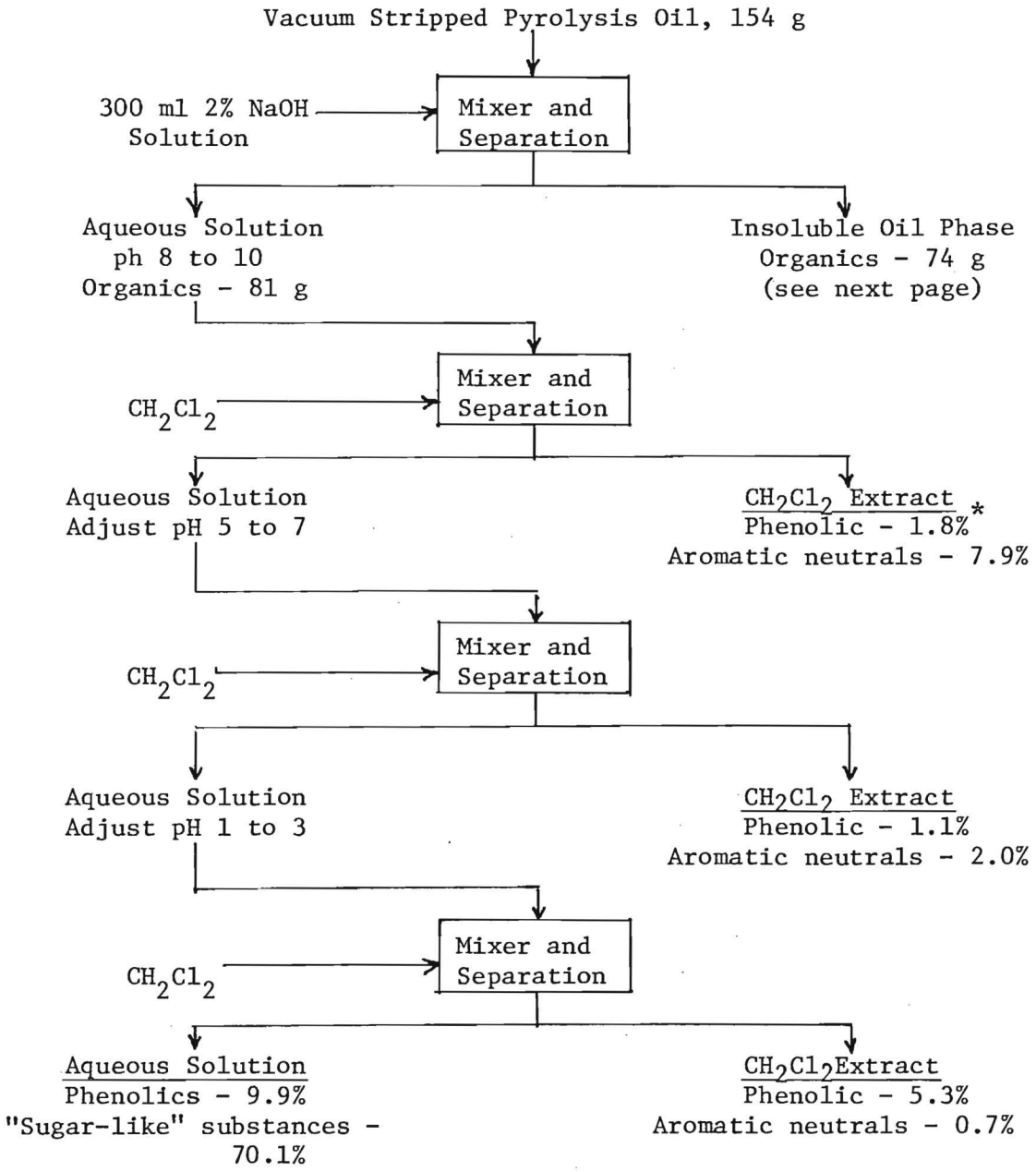
into the anisole fraction, which contained about 62% of the original charge. A good potential step for processing this fraction would be fractional distillation. The oil insoluble fraction, which contained about 8.4% of the original charge, was approximately 85% aromatic neutrals. Fractional distillation is also a good potential method for processing this fraction. The aqueous phase could be treated by the salting out technique with sodium sulfate as shown in Figure 3 to yield a highly concentrated phenolic fraction.

Extraction of Sodium Hydroxide Solution of Oil With Methylene Chloride

A sample of vacuum stripped pyrolysis oil (154 g) was treated with 300 ml of 2% sodium hydroxide solution and approximately 52.6% dissolved. A series of methylene chloride extractions then were made at three different pH ranges. The "insoluble oil phase" upon treatment with additional 2% sodium hydroxide solution, dissolved in 400 ml of the alkaline solution. This solution was subjected to a series of methylene chloride extractions at the same pH ranges. The schematic for these extractions are presented in Figure 6. The yield data are presented in Table 2. An examination of the data shows that phenolics are obtained with methylene chloride at each pH range and approximately 52 of the phenolics remain in the aqueous phase at pH range 1 to 3. The significance of this experiment is that the pyrolysis oil will dissolve in sufficient sodium hydroxide solution which offers the opportunity for a series of extractions at different pH ranges and also with a variety of organic solvents.

Extraction of Organic Solvent Solutions of Oil

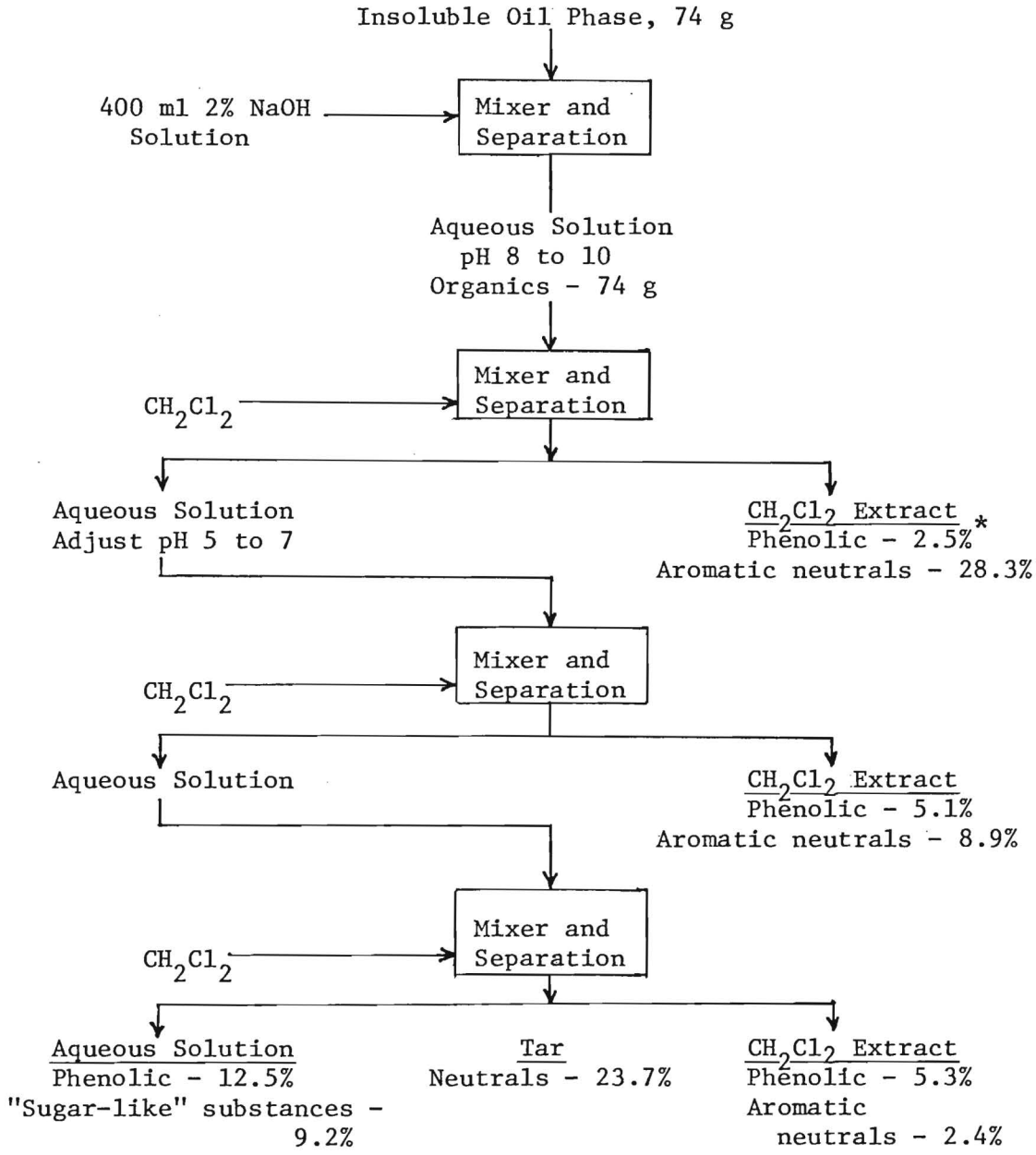
The vacuum stripped pryolysis oil dissolves in methylene chloride and in n-butanol to give clear solutions. Solutions of vacuum stripped oil in methylene chloride were extracted with water and the combined water extracts were then extracted in one experiment with diisopropyl ether and in a second experiment with methyl isobutyl ketone (MIBK). The schematics for these two experiments are shown in Figures 7 and 8. The data are summarized in Table 3. The significance of the data in these experiments is that a fraction of phenolics is obtained with MIBK which contains less than 10% other organics. An examination of the data will also indicate one of the difficulties encountered in working with pyrolysis oils. One would expect the quantity of phenolics



*Percent yield is based on weight of material extracted from 81 g of organics.

Figure 6. Extraction of Pyrolysis Oil With Two Percent Sodium Hydroxide Solution

Vacuum Stripped Pyrolysis Oil, 154 g (cont'd)



*Percent yield is based on weight of material extracted from 74 g organics.

Figure 6. Continued.

Table 2. Yields From Methylene Chloride Extractions of Alkaline Solutions of Pyrolysis Oil

Fraction	First Series CH_2Cl_2 Extractions Weighting	Second Series CH_2Cl_2 Extractions Weighting	Total Yield	% Yield
pH 8 to 10				
Phenolics	1.46	1.85	3.31	2.17
Aromatic neutrals	6.4	20.9	27.3	17.9
pH 5 to 7				
Phenolics	0.89	3.77	4.67	3.06
Aromatic neutrals	1.62	6.59	8.21	5.38
pH 1 to 3				
Phenolics	4.29	3.92	8.21	5.38
Aromatic neutrals	0.57	1.78	2.35	1.54
Aqueous Phase				
Phenolics	8.02	9.25	17.3	11.3
"Sugar-like" substances	56.8	6.81	63.6	41.7
Tar neutrals	--	17.5	17.5	11.8
Totals				
Phenolics	--	--	33.5	21.9
Aromatic neutrals	--	--	37.9	24.8
"Sugar-like" substances	--	--	63.9	41.7
Tar neutrals	--	--	17.5	11.8

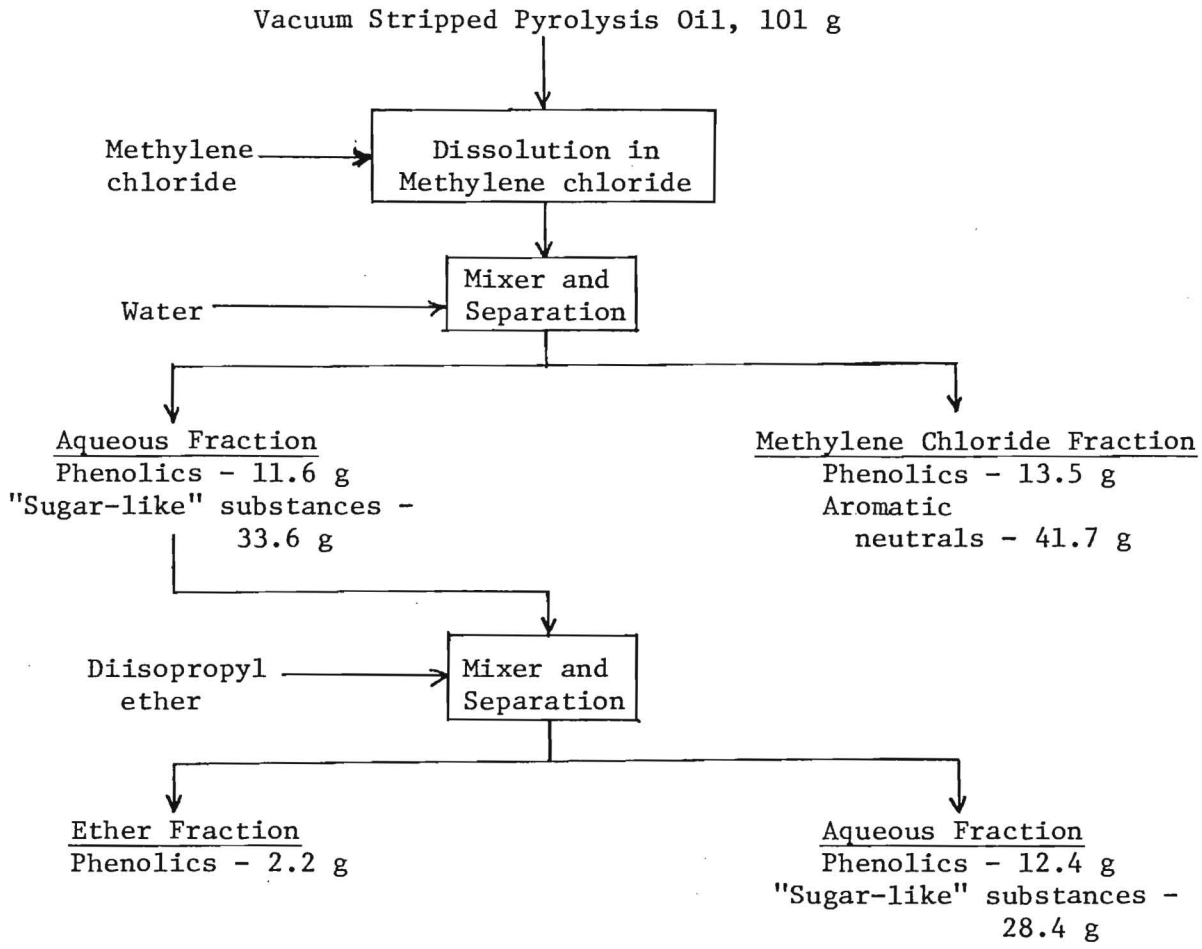


Figure 7. Extraction of Methylene Chloride Solution of Oil with Water Followed by Diisopropyl Extraction of Aqueous Fraction

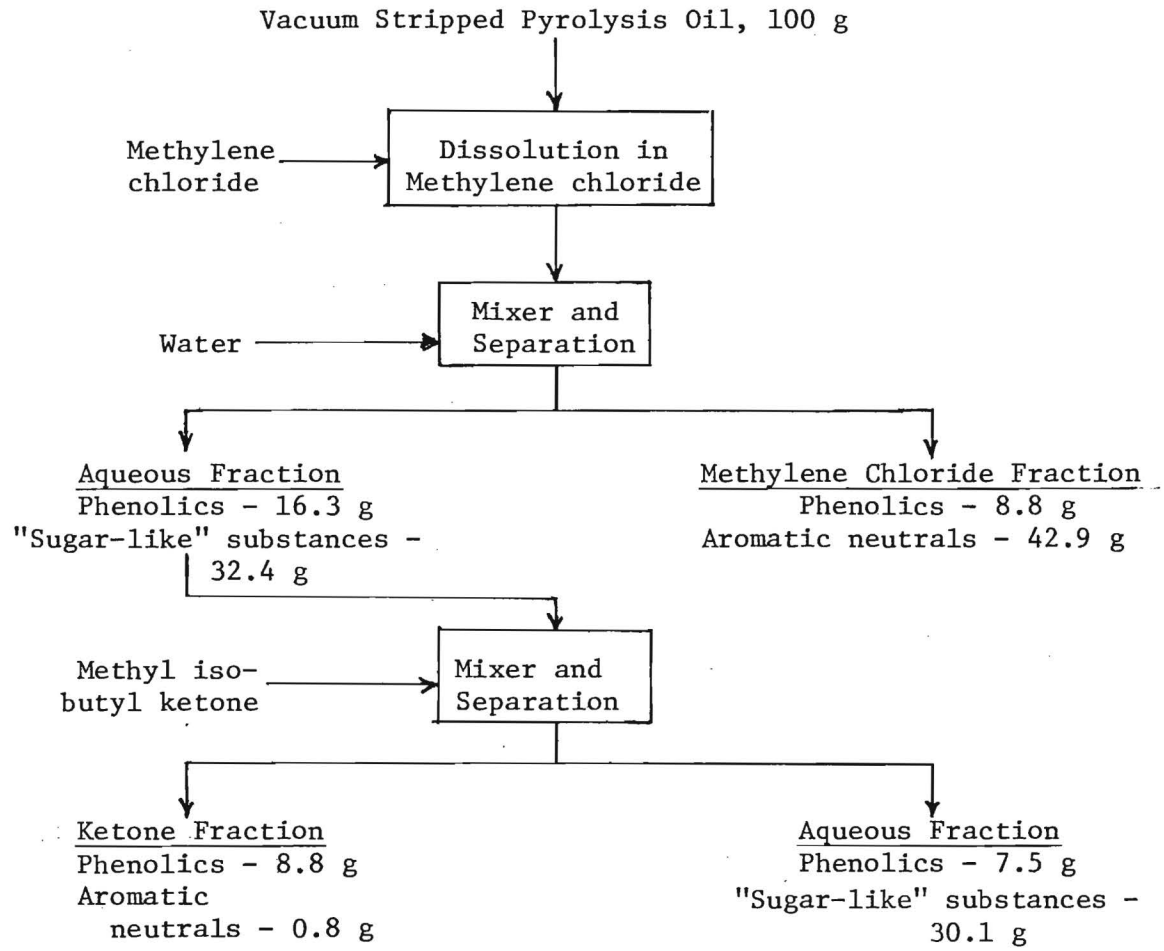


Figure 8. Extraction of Methylene Chloride Solution of Oil With Water Followed by Methylisobutyl Ketone Extraction of Aqueous Fraction

Table 3. Yields in Final Fractions at Separation Techniques Shown Schematically in Figures 6 and 7

Final Fraction	Diisopropyl Ether Experiment	Methylisobutyl Ketone Experiment
Methylene chloride		
Phenolics	13.5 g	8.8 g
Aromatic neutrals	41.7 g	42.9 g
Aqueous		
Phenolics	12.4 g	7.5 g
"Sugar-like" substances	28.4 g	30.1 g
Organic solvent		
Phenolics	2.2 g	8.8 g
Aromatic neutrals	0	0.8 g

in the final methylene chloride fractions to be in closer agreement. The lack of agreement can be attributed to differences in experimental techniques and to the need for improvement in analytical techniques.

The vacuum stripped pyrolysis oil is soluble in n-butanol, and an aqueous extraction experiment with a n-butanol solution of pyrolysis oil was carried out to determine the distribution of the phenolic and other organics between the aqueous and n-butanol fractions. The schematic for this experiment with yields for each fraction are given in Figure 9. The important result of this experiment is the reduced amount of "sugar-like" substances in the aqueous phase as compared with the other extractions with the exception of the sodium sulfate extraction. There is the potential that extraction of a n-butanol solution of pyrolysis oil with sodium sulfate solution could yield an aqueous solution with a high concentration of phenolics relative to other organics. In this experiment, material recovery is not too good because in the removal of the n-butanol at low vacuum, some of the more volatile aromatic compounds were lost.

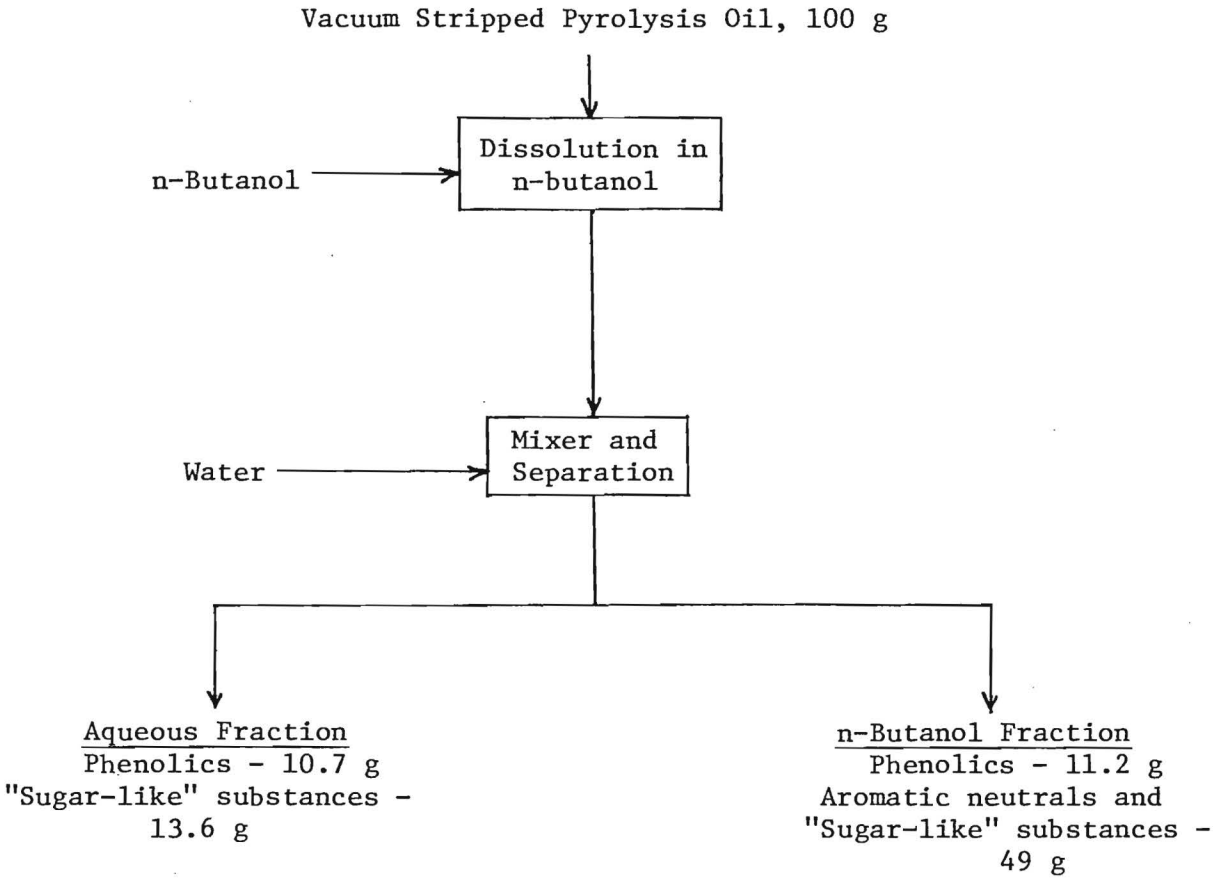


Figure 9. Extraction of n-Butanol Solution of Pyrolysis Oil With Water

SECTION 4

PLANS FOR FUTURE WORK

The major effort during this next report period will be the preparation of a complete report covering the performance period of June 21, 1976 through September 30, 1978.

APPENDIX A

EXPENDITURES

The expenditures from the initiation of the project through May 31, 1978, were as follows:

(a)	Direct wages and salaries	$ 63,361.48
	Retirement (9.35% of applicable wages and salaries)	5,831.85
	Travel	858.26
	Materials and Supplies	6,316.76
	Materials and Supplies (Encumbered)	24.37
	Capital	922.07
	Overhead (68% of direct wages and salaries)	43,085.81
	Total	$ 120,400.60
(b)	Total Budget	$ 130,000.00
	Expenditures through May 31, 1978	$ 120,400.60
	Remaining Funds	$ 9,599.40